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RARE-EARTH SILICATES

COMMUNICATION 1. PHASE DIAGRAM OF THE SYSTEM $\text{La}_2\text{O}_3\text{-SiO}_2$

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 2, pp. 153-156, February, 1960

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The study of the properties of rare-earth elements, their reactions with each other and with other elements, and their use in various fields of the national economy has been developed particularly in recent years both abroad and in the Soviet Union [1-4]. In the foreign literature, many papers have been devoted to the chemistry, metallurgy, and problems in the separation and application of rare-earth elements, and promising developments in this scientific field have been presented. Thus, the U. S. Bureau of Mines planned a large program of fundamental research on the refractory properties of rare-earth oxides individually and in combination with other oxides [5]. The study of phase diagrams of systems containing rare-earth oxides is a new section of the physical chemistry of silicates.

As follows from a review of the literature, the reaction of silica with rare-earth oxides has hardly been studied. In the Institute of Silicate Chemistry, a large program of work has been planned for the study of phase diagrams of systems containing silica and oxides of rare and disperse elements, and the investigation of the physical and physicochemical properties of crystalline and vitreous phases of these systems. The purpose of the present work was a study of phase diagram of the binary system $\text{La}_2\text{O}_3\text{-SiO}_2$.

EXPERIMENTAL

The following materials were used for the preparation of samples: silica in the form of a fine powder (99.90% SiO_2) and lanthanum oxide, containing up to 0.7% of impurities (Nd_2O_3 , CeO_2 , PrO_2 , Ca, Fe). Homogeneous samples were obtained, and specimens quenched and annealed by the procedure we described previously [6]. The samples were investigated under a microscope and by x-ray structural analysis. The refractive indices of highly refractive substances were determined on a modernized MIS-11 microscope.

Since there is a possibility of a change in the valence of lanthanum at high temperatures in a stream of argon, the degree of reduction of La_2O_3 to LaO was checked by two methods: 1) by firing a sample which had been fired in a microfurnace in a tubular furnace and determining the increase in weight (LaO is converted to La_2O_3); 2) by a volumetric method (oxidation of LaO to La_2O_3 with permanganate solution and titration with oxalic acid). As the experiments showed, the LaO content of a sample from pure lanthanum oxide after heating was small and increased with a rise in temperature:

At 1800°	-	0.15 weight %
1900°	-	0.30 "
2000°	-	0.50 "
2100°	-	0.65 "

RESULTS OF INVESTIGATION

The general form of the phase diagram we obtained for the system $\text{La}_2\text{O}_3\text{-SiO}_2$ is given in Figs. 1a and b. As Fig. 1 shows, a chemical compound with the composition $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ (78.3 weight % of La_2O_3 and 21.7 weight % of SiO_2) is formed in the system and layer formation occurs*.

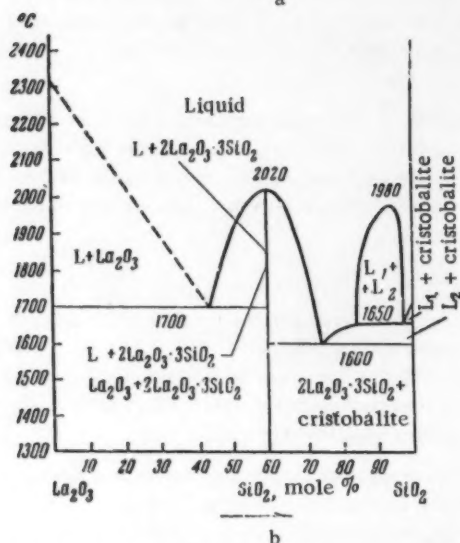
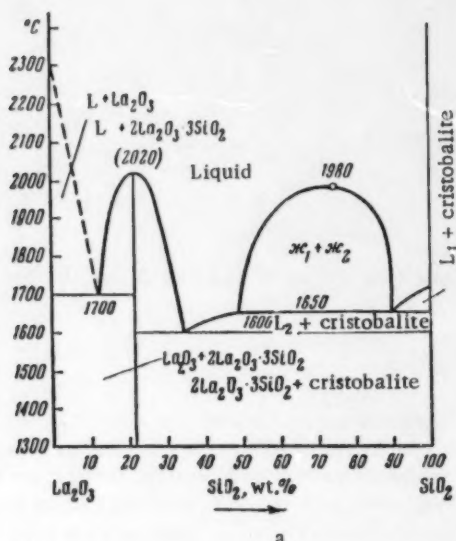


Fig. 1. Phase diagram of the system $\text{La}_2\text{O}_3\text{-SiO}_2$: a) In weight % b) in mol. %.

There are two eutectics in the phase diagram of the system: One is formed between lanthanum oxide and the compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ at 1700° and the composition 87.5 weight % (56.3 mol. %) of La_2O_3 and 12.5 weight % (43.7 mol. %) of SiO_2 ; the second is formed between the compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ and cristobalite at 1600° and a composition of 65 weight % (24.7 mol. %) of La_2O_3 and 35 weight % (75.3 mol. %) of SiO_2 .

The compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$. The compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$, found in the system, melted without decomposition at $2020 \pm 50^\circ$. The rapid crystallization this silicate from the melt made it impossible to quench a melt of this composition in the form of a glass. The compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ belongs to the hexagonal crystal system. Photomicrographs of its crystals are shown in Fig. 2 a and b. Lanthanum silicate separates in the form of hexagonal platelets with white and orange interference colors in polarized light in thin polished sections. The mean refractive index of crystals of this compound equaled 1.85 ± 0.05 . The microhardness, determined on a PMT-3 apparatus, was 655 kg/mm^2 , which corresponds approximately to the hardness of apatite (536 kg/mm^2) and albite (795 kg/mm^2). These correspond to the values 5 (apatite) and 6 (albite) on the Mohs scale.

Figure 3 shows the x-ray diffraction pattern of $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$, obtained with an ionization recorder, and the table gives calculated data for this diffraction pattern. The parameters of the elementary cell of $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ ($\text{La}_4\text{Si}_3\text{O}_{12}$) have the following values: $a = 11.23 \text{ kX}$, $c = 4.674 \text{ kX}$, $c/a = 0.42$. The density determined in kerosene with a pycnometer equaled 5.31 g/cc .

As calculations showed, the elementary cell contained 2 molecules and its density, obtained from x-ray data, equaled 5.303 g/cc . Apparently, $\text{La}_4\text{Si}_3\text{O}_{12}$ has a structure belonging to the olivine group with isolated tetrahedral $[\text{SiO}_4]^{4-}$ anions and is lanthanum orthosilicate, $\text{La}_4(\text{SiO}_4)_3$. The chemical stability of $\text{La}_4(\text{SiO}_4)_3$, determined qualitatively with respect to hydrochloric acid, is very low. As literature data shows, low chemical stability is characteristic of the olivine group.

In Fig. 1 a and b, the layer-formation region is isolated by a binodal curve. The two immiscible liquids (two glasses) are in equilibrium with cristobalite at 1650°

over the concentration range of 50-90 weight % (84.5-97.9 mol. %) of SiO_2 . In this case the equilibrium is monotectic and is determined by the equation $L_2 = L_1 + S$ (cristobalite). The critical point of layer formation lies at 1980° and a composition of 25 weight % (5.8 mol. %) of La_2O_3 and 75 weight % (94.2 mol. %) of SiO_2 .

* It has now been established that two other compounds are formed in the system: $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ with refractive indices $n_D = 1.875$; $n_p = 1.855$; $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ with refractive indices $n_D = 1.762$, $n_p = 1.752$.

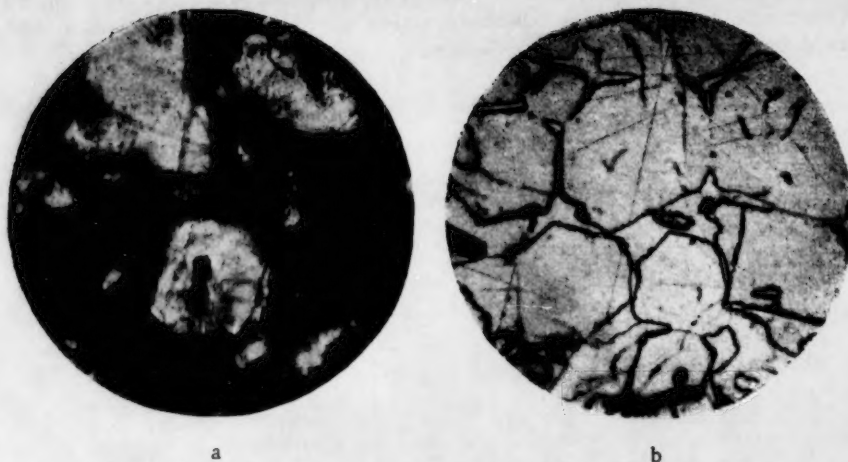


Fig. 2. Photomicrographs of crystals of the compound $2\text{La}_2\text{O}_3\cdot\text{SiO}_2$:
a) Transmitted light, $\times 320$; b) reflected light, $\times 320$.



Fig. 3. X-ray diffraction pattern of lanthanum silicate, $2\text{La}_2\text{O}_3\cdot 3\text{SiO}_2$.



Fig. 4



Fig. 5

Figs. 4 and 5. Photomicrographs showing the formation of two glasses:
4) 60% La_2O_3 , 70% SiO_2 , 1700° ; 5) 20% La_2O_3 , 80% SiO_2 , 1800° .

The separation of one glass in the other can be seen on the microphotographs in Figs. 4 and 5. The more "basic" glass (light) has a certain fluidity and contains cristobalite grains; the more "acidic" glass (dark) differs in viscosity and is found to be free from cristobalite after quenching.

X-ray Diffraction Investigation of Lanthanum Silicate, $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$

No.	d/n	I/I_0 in %	hkl	No.	d/n	I/I_0 in %	hkl
1	3,6791	19	210	20	1,4869	22	203
2	3,3688	34	201	21	1,3687	16	223
3	3,2410	31	300	22	1,3492	16	441
4	2,9470	100	211, 310	23	1,3312	25	432
5	2,8521	31	220	24	1,3154	34	403
6	2,3659	13	002	25	1,2890	46	323
7	2,2400	19	320	26	1,2679	41	413
8	2,1757	25	401, 112	27	1,2170	10	442
9	2,1276	15	202	28	1,1912	22	333
10	2,0345	44	321	29	1,1679	19	004
11	1,9804	34	212	30	1,1585	22	104
12	1,9348	62	411	31	1,1437	19	114
13	1,8825	25	330	32	1,0774	25	224
14	1,8530	44	132	33	1,0533	19	404
15	1,8305	62	420	34	1,0448	28	443
16	1,8142	41	302, 222	35	1,0350	19	324
17	1,5911	25	430	36	1,0192	19	414
18	1,5752	28	412	37	1,0095	25	604
19	1,5263	25	431				

SUMMARY

1. A study of the binary system $\text{La}_2\text{O}_3\text{-SiO}_2$ made it possible to construct the phase diagram.
2. The compositions and temperatures of the invariant points were determined.
3. The compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$, which is lanthanum orthosilicate, $\text{La}_4(\text{SiO}_4)_3$, was synthesized and investigated.
4. The boundaries of the layer-formation region, its upper critical point, and the coexistence temperature of the crystalline phase (SiO_2) and the two liquids (glasses) were established.

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MEAN BOND ENERGIES AND THEIR APPLICATION IN THE CALCULATION OF THE HEIGHTS OF ENERGY BARRIERS OF CATALYTIC REACTIONS

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The method that one of us proposed previously for calculating the height of energy barriers ($-E$) of catalytic reactions which proceed with the intermediate formation of a multiplet complex [1] requires a knowledge of the mean energies of bonds (Q) between the atoms of the reacting substances. Until recently, data presented in Cottrell's monograph [2], where the values were calculated on the basis of the heat of atomization (sublimation) of carbon $A_C = 138$ and nitrogen $A_N = 85.57$ kcal/g-at, were accepted as a summary of the values of Q .

Since the problem of the true values of A_C and A_N and some others, which has been discussed in the literature for a long time, is apparently solved now [3], it is necessary to have a summary of recalculated values of Q , though this calculation has no effect on the values of $-E$ (see below). Then, having reliable thermochemical data, it may be possible to turn to the calculation of more individualized values of Q , depending on the nature of the chemical compound, the position of the atoms in the carbon chain of the organic molecule, the presence of strain in rings, the conjugation of bonds, additional stabilization, etc. This route may gradually lead to the discovery of the effect of "extraskeletal substituents" [1] on the energy of the bond with the catalyst and the value of $-E$. It is possible to use Tatevskii's method [4] or some other, simpler method for obtaining individualized values of Q .

We undertook to calculate Q for various compounds. We based our calculations on the values $A_C = 171.3$ and $A_N = 113.0$ kcal/g-at (25°). As was to be expected, some of the values of Q obtained practically coincided with those presented in the recently published work of Kondrat'ev [3], while the others were calculated for the first time. The calculation was carried out according to the usual additive system; the values obtained refer to the vapor state under standard conditions. The thermochemical data were taken from the latest handbooks [5] or later original works. When a sufficiently large amount of data was available, the values of Q obtained were the mean result of calculations for 8-12 substances of a homologous series. They were checked by resubstitution. Here we also introduced available data for other homologs. As a result, slight corrections were sometimes introduced so that the values of Q obtained were suitable for most members of a homologous series (for example, instead of $Q_{C-H} = 98.75$ kcal).

The values of Q for the bonds $C_{arom}-C_{arom}$ and $C_{arom}-H$ were found by solution of a system of two equations, derived by means of the additive system for benzene and biphenyl,* and those for the bonds $C_{arom}-C_{aliph}$ were obtained by substituting the values thus obtained in corresponding equations derived for propyl-, butyl-, and amylbenzene, the compatibility of which was checked algebraically. By proceeding in this way it was possible to obtain two series of values for the bond energies mentioned above, depending on whether it was considered that all the $C_{arom}-C_{arom}$ and $C_{arom}-H$ bonds in benzene and biphenyl are identical (variant I) or it was considered that the latter compound has an additional stabilization energy (greater than two benzene rings) of ~ 7.5 kcal (variant II). We chose variant I as the values of Q obtained in this case formed a sequence which

*The standard heat of formation for biphenyl was taken as equal to -39.6 kcal/mole according to [6].

was symbatic with the sequence of the dissociation energies of the same bonds [3, 7] and also the value of $Q_{C_{arom}-C_{arom}}$ obtained was closer to that calculated from the degree of double bonding of carbon in benzene. As regards the value of $Q_{C_{arom}-O}$, due to the lack of data on the heat of combustion of phenol as a vapor or on its heats of fusion and evaporation, the indirectly derived and approximately calculated values have an accuracy of no more than $\pm 5-7\%$. There are no completely reliable data on the heats of combustion of Cl, Br, and I derivatives of benzene in the vapor state. For calculating the values of $Q_{C_{arom}-Hal}$ we used data presented by Hartley et al. [8], which agrees well with more recent data [9], and values of the heat of evaporation from [10]. Considering what has been said, it must be borne in mind that the values of $Q_{C_{arom}-Hal}$ found may be corrected later, though evidently by not more than 1-2 kcal. $Q_{C_{arom}-N}$ was found from data for aniline.

The values of the energies of conjugated double bonds in dienes and trienes and of single C-C bonds lying between conjugated bonds were calculated by solving a system of equations derived by the additive system for 1,3-butadiene, 1,3-pentadiene, and 1,3,5-hexatriene with the assumption that the values of these bonds in all these compounds are identical and that the mean energies of the other bonds retain their normal values (data from [11] were used for the calculation).

The energies of C-C bonds in 3-, 4-, and 5-membered cyclanes were found from the heats of combustion of corresponding unsubstituted hydrocarbons [12, 13] and the C-O bond energy in ethylene oxide was found on the assumption that $Q_{C=C}$ in $(CH_2)_2O$ has the same value as in cyclopropane. The value of Q_{C-H} in all these compounds was taken as 98.75 kcal. The results of calculating the values of Q (in kcal) are given below in Tables 1 and 2. The accuracy of the values given in the tables may be assessed from the mean absolute error δ (in kcal) and the relative error Δ (in %), found when the values were checked by resubstitution, i.e., when the heat of formation (ΔH) of the given compound was calculated from the values in the tables and then compared with data in handbooks or original work. Thus, for C_2-C_{20} normal paraffins, $\delta = \pm 0.3$, $\Delta = \pm 0.5$ (the sign \pm will subsequently be omitted). For C_3-C_{20} normal α -olefins, $\delta = 0.3$, $\Delta = 1.0$; for normal β -olefins (separately for cis and trans isomers), $\delta = 0.5$, $\Delta = 1.5$. For olefins with a branched chain and the double bond other than at the first C-atom, $\delta = 0.8$, $\Delta = 5.5$. For C_2-C_8 normal aliphatic alcohols, $\delta = 1.1$, $\Delta = 1.85$. For C_2-C_3 aldehydes, $\delta = 0.7$, $\Delta = 2.2$. For C_3-C_6 ketones, $\delta = 1.3$, $\Delta = 4.2$. For C_6-C_{22} aromatic and aliphatic-aromatic hydrocarbons, including 1,4-substituted alkylbenzenes, styrene, and biphenyl, $\delta = 0.7$ (for a total of 21 compounds); calculation of the relative error for 15 of the 21 compounds gave $\delta = 0.75$ and $\Delta = 1.8$, while for the other 6 compounds, the numerical values for which were small, $\Delta = 18$ though δ for them was only 0.6.

TABLE 1. Mean Energies of Single Bonds (in kcal)

Atomization energy	171.3	52.09	113.0	59.5	—	29.0	26.7	25.5
Atoms	C_{aliph}	H	N	O	C_{arom}	Cl	Br	I
C_{aliph}	82.87							
H	98.75	104.18						
N	69.0	93.4	75.33					
O	85.5	110.8	75.5	59.5				
C_{arom}	95.2	108.1	85.2	97.5	112.0			
Cl	79.2	103.1	37.9	49.6	93.2	58.0		
Br	66.6	87.4	—	—	79.2	—	53.4	
I	52.4	71.3	—	—	65.1	—	—	51.0

However, the values of Q we calculated have another unknown inaccuracy for the two following reasons: Firstly, the sparseness and often the inadequate accuracy of the data on heats of combustion, for example, for oxygen-containing organic compounds, and secondly, the fact that they give no reflection of small structural characteristics (isomerism, etc.) and the effect of neighboring atoms and groups in relation to their disposition.

*n-Propyl-, 1-methyl-4-ethyl-, 1,2,4-trimethyl-, n-butyl-, tert-butyl-, and 1,2,3,4-tetramethylbenzene.

As thermochemical data accumulate and are refined, both these difficulties may be overcome by calculation of individualized values of Q , as we have already mentioned above. With an increase in the accuracy of the values of Q , their value will become increasingly greater and the possibilities of application will be extended.

TABLE 2. Mean Energies of Multiple and Some Other Bonds (in kcal)

Bond	Compounds	Mean bond energy
C=C	In normal α -olefins	146.2
C=C	In normal β -olefins (mean for cis and trans forms)	148.2
C=C	In γ -olefins (as above)	148.4
C=C	In branched-chain olefins other than α -olefins	151.5
C \equiv C	In alkanes	199.9
C Δ -C Δ	In cyclopropane	73.8
C \square -C \square	In cyclobutane	76.4
C \square -C \square	In cyclopentane	81.7
O=O	In O ₂	119.0
-O-O-	In H ₂ O ₂ and organic peroxides	33.4
C=O	In aldehydes	173.0
C=O	In ketones	180.6
C Δ -O	In ethylene oxide	76.9
N=O	In nitro compounds	103.2
N \equiv N	In N ₂	226.0
C \equiv N	In a number of compounds containing the CN group	204.3

Footnote: 1. The value of $Q_{C=C}$ presented above for branched-chain olefins other than α -olefins gives a more satisfactory result than 146-148 kcal in most cases, but not always.

2. The value of $Q_{C=C}$ for conjugated bonds in di- and triolefins with a normal chain equals 149 kcal and $Q_{C-C} = 82$ kcal for single bonds lying between the conjugated bonds.

Application of mean bond energies to the calculation of the height of energy barriers of reactions. There have already been a number of cases where values of Q have been used successfully in the calculation of the height of energy barriers of catalytic reactions which proceed with the intermediate formation of a multiplet complex and also in the calculation of the energy of a bond between a catalyst and atoms of reacting molecules (see, for example [14, 17]). We recently made similar calculations, using individualized values of Q , which were obtained with allowance for bond strain arising with 3-, 4-, and 5-membered ring systems of carbon atoms [18, 19]. Two more examples of possible calculations are given below.

Energy barrier in the hydrogenolysis of halogen derivatives of hydrocarbons on an activated carbon catalyst. Patrikeev and one of us [20] previously calculated the height of the energy barrier of the desorption state of this reaction ($-E^*$) for a number of cases. Calculations with the aid of the new values of Q confirmed the previous deductions and also explained the low degree of replacement of Br by H in C₆H₅Br, which is observed experimentally (see Table 3).

TABLE 3. Hydrogenolysis of Halogen Derivatives of Hydrocarbons

Substance undergoing hydrogenolysis	$-E^*$ in kcal	Deg. of replace. of halogen at 400° accord. to [20] in %
C ₆ H ₅ Br	199.8	3.0
CHCl ₃	157.7	18.2
n-C ₄ H ₉ Br	144.7	42.0

Sequence of reactions in the dehydrogenation of various aliphatic alcohols on the same catalyst. If it is assumed that the adsorption stage is the limiting stage in these reactions, then the height of the energy barrier when the reaction proceeds by a doublet mechanism can be calculated from the formula:

$$E^* = -Q_{C-H} - Q_{C-O} + 2Q_{H-K} + \\ + Q_{C-K} + Q_{O-K} = -Q_{C-H} + M,$$

where $M = +2Q_{H-K} + Q_{C-K} + Q_{O-K} - Q_{C-O}$ and K is the catalyst.

As one of us showed previously [21], the limiting stage in the dehydrogenation of alcohols is rupture of the C-H bond on the catalyst. Bearing this in mind, in the first approximation we can assume that $M = \text{const.}$ for alcohols of a homologous series. In addition, as an approximation we will assume that the energy of a C-H bond in a methyl radical is the same as in methane (99.4 kcal). Then, by first calculating the values of Q in CH_2 groups adjacent to the hydroxyl by the additive system, we can find the sequence of reactions for different alcohols from the ease of their dehydrogenation. The results of the calculation are given below in Table 4 in comparison with experimental data from [22], where precipitated copper was used as the catalyst.

TABLE 4. Dehydrogenation of Aliphatic Alcohols

	Alcohols				
	<i>i</i> -C ₄ H ₉ OH	C ₃ H ₇ OH	C ₂ H ₅ OH	<i>n</i> -C ₄ H ₉ OH	CH ₃ OH
Value of $Q_{\text{C-H}}$ in kcal	94,9	96,8	98,0	98,4	99,4
Rate of H_2 liberation under identical exptl. cond. at 182° in ml/hr	1520	219	340	281	100
Activation energy in kcal/mole [22]	6,03	15,01	12,14	12,42	21,86
Activation energy in kcal/mole [23] (oxide catalyst)	12,8	15,9	15,6	16,3	—

With all the unavoidable approximateness of such a calculation, the very possibility that it can be made is of definite interest. Table 4 shows that there is only one case of a discrepancy between experiment and calculation. This is explained by the inadequacy of the latter, though the inaccuracy of the thermochemical data could also play a part.

According to theory [23], the effect of substituents which we attempted to elucidate by the calculation given should only be expected when a substituent has a different action on the energy of the bond with the neighboring atom in the reacting molecule and with the catalyst, i.e., $Q_{\text{C-H}}$ and $Q_{\text{C-K}}$. Thus, if the value of $Q_{\text{C-H}}$ increases under the action of the substituent and the value M remains constant, the height of the energy barrier also increases. For any catalyst where there is a similar uncompensated effect of the substituents, the sequence of the dehydrogenation of alcohols (from the activation energies of the reactions) must remain the same. In actual fact, in [23] experiment showed the same sequence with the same (though not so marked) single exception, namely, ethyl alcohol* (see Table 4).

In conclusion we should emphasize the following fact. In previously published work the values of $-E$ were calculated from data in Cottrell's summary and from [24]. The values of Q are naturally strongly dependent on the heats of atomization of the elements. Nonetheless, as was shown in [1], it is also very important that the heights of energy barriers of the reactions ($-E$) are independent of the numerical values of the heats of atomization (A), as corrections in the latter compensate each other. Therefore, there is no need for recalculation of values of $-E$ found previously.

SUMMARY

1. The latest and most reliable data on heats of atomization were used for calculating the mean values of interatomic bond energies by the additive system. New or refined values were obtained in 22 cases.
2. A method was proposed for the approximate calculation of bond energies by solution of a system of equations, derived by the additive system for similar substances and containing the required values as unknowns.
3. Examples are given of the use of the bond energies found in the calculation of the height of energy barriers of reactions.

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PHASE COMPOSITION, STRUCTURE, AND MAGNETIC PROPERTIES OF COPRECIPITATED FERRIC OXIDE-ALUMINA GELS

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The study of the state of the components in binary systems and the structures of their constituent phases has been the subject of a number of recent papers [1-4] in which the phenomena of mutual solution and prevention of crystallization in some form or other have been studied. Such investigations are of considerable interest from the point of view of methods for preparing mixed catalysts and elucidating the nature of their activity and selectivity of action. An example of this is a detailed investigation of the catalytic properties of the system $\text{NiO-Al}_2\text{O}_3$ [5] in relation to phase composition and structure.

It is well known that both Al_2O_3 and Fe_2O_3 individually are catalysts of many reactions. However, binary catalysts with the composition $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ are also used for the conversion of CO with steam [6], for the dehydration of alcohols and their codehydration with ammonia or amines [7], and for the hydrolysis of esters [8]. The study of the system $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ is of particular interest in connection with the polymorphism of its components and possible phase conversions, which can be followed by x-ray diffraction methods for both components and magnetochemically for phases containing iron. Our article is devoted to such an investigation, in which a study was made of the effect of component ratio and thermal treatment conditions on the phase composition and structure. All the samples prepared were also studied for adsorption properties and catalytic activity in the decomposition of isopropyl alcohol; these two parts of the investigation are the subject of separate communications.

Information in the literature on the system considered may be summarized as follows. The phase conversion $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ was studied by de Boer and Selwood [9], who found that the activation energy of the process depends on the conditions of the thermal treatment of $\gamma\text{-Fe}_2\text{O}_3$ and also that Al^{3+} ions, which are smaller than Fe^{3+} ions, increase the stability of $\gamma\text{-Fe}_2\text{O}_3$, while larger ions (La) decrease it. The reverse conversion $\alpha \rightarrow \gamma$ was studied by Finch and Sincha [10] (at temperatures up to 900°), who found that it proceeds through the intermediate β -phase ($\sim 500^\circ$), which has certain magnetic anomalies (parasitic ferromagnetism and susceptibility independent of temperature). The properties of a number of binary systems containing Fe_2O_3 and obtained by heating mixtures of oxides were studied by Hüttig [11-13], who showed that in the region of $600\text{-}800^\circ$ there were sometimes sharp changes in magnetic susceptibility, which he explained by the formation of intermediate compounds that may not have a specific x-ray diffraction pattern. Selwood et al. [14] studied Al_2O_3 with iron oxide deposited on it and found that iron was in the form of Fe^{3+} , but with a low magnetic moment of $4.0\text{-}4.4 \mu\text{B}$ instead of $5.9 \mu\text{B}$, which they explained by exchange demagnetization and the intercation covalent bond Fe-Fe , present as a result of this. The formation of a solid solution of $\gamma\text{-Fe}_2\text{O}_3$ in $\gamma\text{-Al}_2\text{O}_3$ was studied by Cirilli [15], who found that in the region of 50-70 weight % of Fe_2O_3 for samples fired at $600\text{-}850^\circ$, there was a sharp jump in the susceptibility, which disappeared at 1000° or with a further increase in the Fe_2O_3 concentration as a result of the formation of the weakly magnetic $\alpha\text{-Fe}_2\text{O}_3$.

EXPERIMENTAL

Materials for investigation. Ferric oxide-alumina gels with various Fe_2O_3 contents were prepared in our laboratory by Pribytkova by coprecipitation of aluminum and iron hydroxides from 10% solutions of their nitrates (in appropriate amounts for the given composition ratio) with ammonia at 20° and a final pH of 9. Each of the

mixtures of hydroxides was dried at 120° after careful washing and then divided into 4 parts, which were then fired for 7 hr each at 400, 600, 750, and 1000°, respectively; the preparations obtained in this way formed the four main series of coprecipitated ferric oxide-alumina gels. These preparations were investigated both before and after catalytic experiments. The Fe_2O_3 content of the starting samples of the series fired at 400° was determined colorimetrically and the results are given in the table. For comparison purposes we also prepared pure Fe_2O_3 and 1) an equimolecular mixture of $\gamma\text{-Al}_2\text{O}_3$ and Fe_2O_3 , ground to a fine powder, part of which was fired at 400° and part at 1000°, and 2) coprecipitated Al-Fe hydroxide, which contained 38 weight % of Fe_2O_3 after firing for 7 hr at 200°, that was divided into separate portions, which were fired at 350, 450, 500, 550, and 575°, respectively, for 7 hr each. This series was called the "temperature section."

X-ray diffraction determination procedure and experimental data.* X-ray diffraction patterns for all the coprecipitated ferric hydroxide-alumina gels (table) and the mechanical mixture were obtained in KMSP monochromator-cameras [16] with $\text{Cu K}\alpha$ radiation. The diffraction lines were recorded on Agfa-Laufilm, 400 mm long, by the asymmetric method over a range of reflection angles from 12°30' to 80°; The dispersion of these x-ray diffraction patterns was evaluated by photometric measurements made with an MF-4 recording microphotometer. X-ray diffraction patterns of the "temperature section" series and the main series after catalytic experiments were obtained in RKD cameras (cassette diameter 57.3 mm) with $\text{Co K}\alpha$ radiation. The intensities of the lines on the x-ray diffraction patterns were assessed visually against a scale of nine. The interplanar distances in the lattices were calculated from data from measurements on x-ray diffraction patterns of Fe_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ with an accuracy of ± 0.002 Å at high values of the angle, while the parameters of the $\gamma\text{-Al}_2\text{O}_3$ lattice were obtained with an accuracy of ± 0.03 Å (due to the diffuseness of the lines and the high dispersion) and those of the $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ lattices were obtained with an accuracy of ± 0.01 Å.

As examples, in Fig. 1 we show x-ray diffraction patterns (reduced by a factor of 4 linearly) of catalysts fired at 600 and 1000°, obtained in KMSP cameras. Data on the phase composition and the values of the parameter a of the crystal lattices of the phases are given together in the table, the second part of which gives data on the phase composition of the catalysts after catalytic experiments had been carried out on them. The numbers of the x-ray diffraction patterns in Fig. 1 correspond to the numbers in the table. Figure 1, in which the phases and the indices of the reflection planes are given, shows that there was a phase conversion close to 1000°; in catalysts of the 400, 600, and 750° series, the Al_2O_3 was in the γ -form, while in the 1000° series it was already in the α -form, even though this temperature is below that of the conversion $\gamma \rightarrow \alpha\text{-Al}_2\text{O}_3$ for the pure oxide. Moreover, Fig. 1 shows that a rise in firing temperature led to coarsening and ordering of crystals of both phases, as the lines increased in number and became thinner; the increase in the number of lines in the range 750-1000° is also a consequence of the phase conversion just mentioned. The table also shows that before use in catalytic experiments, the catalysts of all series consisted of two phases whose parameters differed from those of the pure phases (components); this phenomenon will be discussed in more detail below. In the case of catalysts on which $i\text{-C}_3\text{H}_7\text{OH}$ had been decomposed, with the exception of sample 1, all the catalysts of the 400° series contained the phase Fe_3O_4 instead of Fe_2O_3 , indicating that reduction occurred. The phase Fe_3O_4 was also detected in some of the catalysts of the 600° series; no volume phase of Fe_3O_4 was detected in the other catalysts of this series or the catalysts of the 750° series. The linear dimensions of the crystals of the $\alpha\text{-Fe}_2\text{O}_3$ phase, calculated by the Selyakov-Scherrer formula from microphotometric measurements on the x-ray diffraction patterns, changed little in each series and were 125 ± 25 Å on the average in the 600° series and 150-200 Å in the 750° series. This phase was amorphous to x-rays in catalysts of the 400° series.

As regards preparations of the temperature section, they gave the following picture for the phase composition: 110°-bayerite; 350°- $\gamma\text{-Al}_2\text{O}_3$ and possibly $\gamma\text{-Fe}_2\text{O}_3$ (weak line with $d = 2.07$ Å); 450°- $\gamma\text{-Al}_2\text{O}_3$; 500°- $\gamma\text{-Al}_2\text{O}_3$ and weak lines of $\alpha\text{-Fe}_2\text{O}_3$; 575°- $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. The crystalline phase $\alpha\text{-Fe}_2\text{O}_3$ appeared in this series at 500°.

Method and results of magnetic measurements. In this part of the work, the weight and not the molar content of Fe_2O_3 was used for comparison purposes. The measurements were carried out on the apparatus with anti-magnetic microbalances of type MV-20 (sensitivity $1 \cdot 10^{-5}$ g) by Faraday's method with 0.2 g samples at 20, 80, and 160° and, in addition, thermomagnetic curves were plotted up to 350°. The optical scale of the balances was used for taking readings with time in the susceptibility measurements. The relation between the susceptibility χ and the field strength was checked over the range $H = 1000\text{-}4000$ gauss. Where possible, the values of the Weiss constant Δ were calculated with an accuracy of $\pm 15^\circ$, while the magnetic moments μ were obtained from measurements of χ at various temperatures with an accuracy of ± 0.1 μB (Bohr magnetons).

* Obtained with the assistance of L. D. Kretalova.

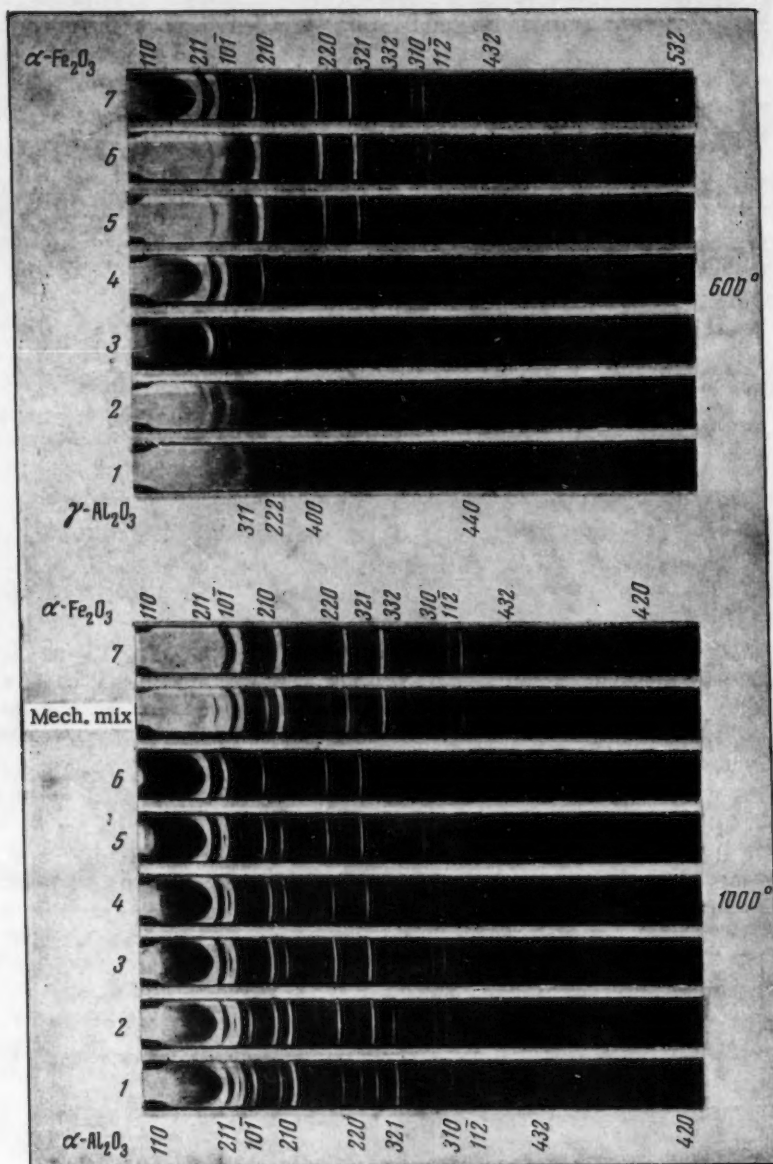


Fig. 1

Phase Composition and Lattice Parameter a of Phases (in Å)

Catalyst No.	Composition		Phase composition and lattice parameters before catalytic experiments										Phase composition after catalytic experiments		
	in weight %		in mol % Fe_2O_3	400° series		600° series		750° series		1000° series		400° series	600° series	750° series	
	Al_2O_3	Fe_2O_3		$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$				
0	100	0	0	7,89	—	—	—	7,87	—	—	—	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	
1	87,8	12,2	8,2	7,93	—	7,91	—	7,92 _s	—	5,16	—	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	
2	74,7	25,3	17,8	7,93	—	7,91	—	7,92 _s	—	5,16	5,39	Fe_3O_4	Fe_3O_4	$\alpha\text{-Fe}_2\text{O}_3$	
3	58,0	42,0	31,6	7,91	—	7,91	—	7,89	5,37	5,16	5,37	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	
4	49,3	50,7	39,6	7,92 _s	—	7,91	5,38	7,88	5,38	5,16	5,38	Fe_3O_4	$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	
5	43,1	56,9	45,7	7,92	—	7,92	5,37	7,91	5,37	5,16	5,39	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	
6	22,2	67,8	57,3	7,93	—	7,93	5,39	7,92	5,37	5,16	5,39	Fe_3O_4	Fe_3O_4	$\alpha\text{-Fe}_2\text{O}_3$	
7	0	100	100	—	5,42	—	5,38	—	5,41 _s	—	5,41 _s	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	
Mechanical mixture 1:1				7,88	5,42	—	5,43	—	—	5,14	5,42	Fe_3O_4	$\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	

Catalysts of the 400° series, before use in catalytic experiments, were paramagnetic and their magnetic properties obeyed the Weiss-Curie law. Figure 2, shows the change with composition of the susceptibility per g of sample (χ_{sam}) and per g of Fe (χ_{Fe}); the nonlinear curves are antipathetic up to 40 weight % of Fe_2O_3 ; then there is a region of symbatic changes with a maximum and a minimum of 58 weight % of Fe_2O_3 . Figure 2, b gives the course of the changes in μ and Δ with catalyst composition; Δ increases with an increase in Fe_2O_3 content, while μ falls from 3.9 at 12.2% of Fe_2O_3 to 2.5 μB at 67.8% of Fe_2O_3 . The curve for μ has anomalies at 50.7 and 67.8% of Fe_2O_3 , corresponding to the maxima on the curves in Fig. 2, a; at these points, the value of μ equals that for the previous Fe_2O_3 concentration. After these catalysts had been used for the decomposition of $i-C_3H_7OH$, they became strongly ferromagnetic and the values of their susceptibility increased sharply (up to 700-800-fold) (Fig. 2, c).

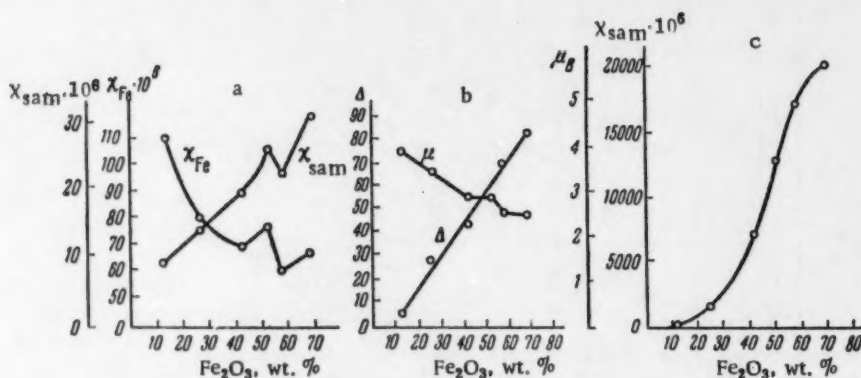


Fig. 2

The starting catalysts of the 600° series differed sharply from those of the 400° series; only two of them (those with 12.2 and 25.13% Fe_2O_3) were paramagnetic, while the others were strongly ferromagnetic with maxima on the susceptibility curves. After catalytic experiments, χ for preparations of this series also increased, as can be seen from Fig. 3, a, though to a lesser extent than in the 400° series. Figure 3, b shows thermomagnetic curves of the ferromagnetic catalysts of the 600° series, measured up to 350°; the Curie point (c) is clearly seen on the curve for the change in χ for the catalyst with 42.3% Fe_2O_3 at ~80°. There is also a Curie point on the curve for the catalyst with 59.6% Fe_2O_3 where the value of χ falls most sharply with temperature.

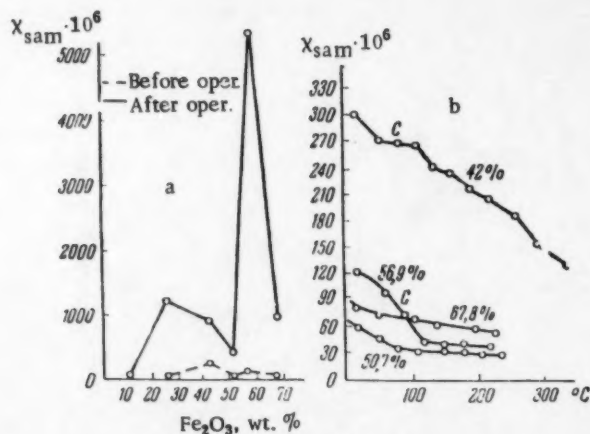


Fig. 3

750° series. Only one of the starting catalysts was paramagnetic and the rest were ferromagnetic. The change in χ with the composition of the preparations was, in general, analogous to the changes in the 600° series. There was a sharp maximum in χ at 57% Fe_2O_3 and a small maximum at 25%. On the thermomagnetic curves of these preparations there was a sharp fall in susceptibility in the low temperature region and the Curie point lay in the region of 60-80°. Due to their similarity to the curves in Fig. 3, b, the curves for the 750° series are not given. For the other samples of the 750° series, χ changed approximately linearly with temperature. Only a slight increase in χ was observed in the 750° series after catalytic experiments.

Firing catalysts 2-6 at 1000° gave ferromagnetic preparations with a low value of $\chi_{\text{sam}} \approx 22$; χ_{Fe} fell with an increase in the Fe_2O_3 content of the catalysts, indicating an increase in exchange interaction between Fe^{3+} ions. Thermomagnetic curves in this series were anomalous and had hysteresis in the first heating-cooling cycle, which disappeared in subsequent cycles (Fig. 4). Similar anomalies were observed previously [17] in a study of solid solutions of sesquioxides with the participation of iron; they, like parasitic ferromagnetism, are characteristic of $\alpha\text{-Fe}_2\text{O}_3$, whose presence in the samples investigated was demonstrated by x-ray methods. We should note that we also observed anomalous thermomagnetic curves (approximately constant χ at different temperatures as in the case of the second cycle for the 1000° series) in the case of the $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ equimolecular mechanical mixture, fired at 400°, and also pure $\alpha\text{-Fe}_2\text{O}_3$.

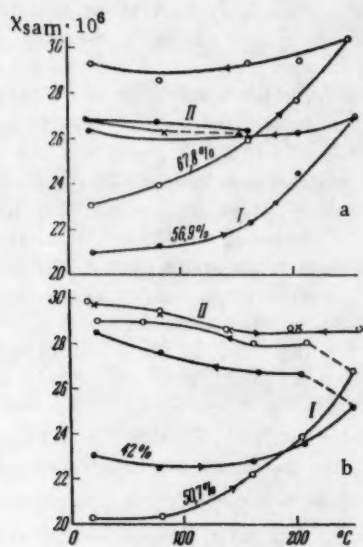


Fig. 4

In connection with the difference in the magnetic properties of the 400, 600, and 750° series and also the phases $\gamma\text{-Fe}_2\text{O}_3$ (ferromagnetic) and $\alpha\text{-Fe}_2\text{O}_3$ (antiferromagnetic with parasitic ferromagnetism), for examining the experimental results it was important to determine the magnetic properties of preparations from the temperature section. As Fig. 5 shows, the magnetic moment μ remained approximately constant within the limits of experimental error of about $\pm 0.2 \mu\text{B}$, while the change in the constant Δ with firing temperature had a minimum corresponding to samples fired at 400-500°, showing that the crystalline phase $\alpha\text{-Fe}_2\text{O}_3$ began to form close to 500°.

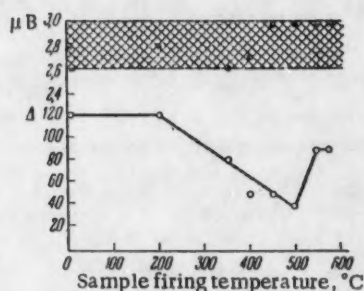


Fig. 5

EXPERIMENTAL RESULTS

A comparison of the results of the phase analysis on ferric oxide-alumina gels of the 1000-degree series with those of the other series shows that even at 1000° cubic $\gamma\text{-Al}_2\text{O}_3$ changed into rhombohedral $\alpha\text{-Al}_2\text{O}_3$ even though, as the literature shows, this phase conversion for Al_2O_3 occurs at 1100° and above. Thus, the experiments showed that the presence of Fe_2O_3 reduced the temperature of the $\gamma \rightarrow \alpha\text{-Al}_2\text{O}_3$ phase conversion. In the case of coprecipitated gels this should be connected with the composition of the Al_2O_3 phase. As has already been noted, the starting gels fired at 600° and above consisted of two phases, which are arbitrarily denoted as $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ in the table. A more detailed characterization of them was obtained by determining the crystal lattice

parameters both from our experimental data and from literature data: γ - Al_2O_3 has $a = 7.89$ - 7.90 Å, α - Al_2O_3 has $a = 5.13$, and α - Fe_2O_3 has $a = 5.41$ Å. As is shown by the data in the table, the lattice parameter of the γ - Al_2O_3 phase of the mixed gels has the high value of 7.92 - 7.93 Å and the parameter $a = 5.16$ Å for the α - Al_2O_3 phase of the 1000° series. This increase in the parameter is the result of the formation of a solid solution of Fe_2O_3 in Al_2O_3 , since the radius of the Fe^{3+} ion is 0.67 Å, while the radius of the Al^{3+} ion is 0.57 Å. From the fact that the lattice parameter of Al_2O_3 in the samples investigated does not vary with the concentration of the second component (Fe_2O_3) in them, it follows that the phases α - and γ - Al_2O_3 are saturated solid solutions of Fe_2O_3 in the corresponding Al_2O_3 . What has been stated also refers to the ferric oxide-alumina gels fired at 400° in which no independent crystal phases of Fe_2O_3 were detected. The concentration of Fe_2O_3 in these solid solutions, calculated by Vegard's rule [18] were 8 mol. % in the case of γ - Al_2O_3 and 11 mol. % in the case of α - Al_2O_3 .

On the other hand, the lattice parameter for the α - Fe_2O_3 phase in the samples investigated was low and this is explained by the solution of Al_2O_3 in it. This is confirmed by the fact that preparations of the mechanical mixture, in which mutual solution was hampered in comparison with the case of coprecipitated gels, had values of a corresponding to those of pure γ - and α - Al_2O_3 and α - Fe_2O_3 (table). According to literature data [19-21], α - Fe_2O_3 dissolves up to 25 mol. % of Al_2O_3 , but in our case solid solutions with up to ~ 10 mol. % of Al_2O_3 were formed. Thus, the phases given in the table which retain the structural features of the main component are the solid solutions just described. Our experiments confirmed again the limited mutual solubility of Al_2O_3 and Fe_2O_3 and the absence of a continuous series of solid solutions.

The next problem to be discussed is the possibility of the presence of γ - Fe_2O_3 in the ferric oxide-alumina gels studied. It is known that γ - Fe_2O_3 , which is strongly ferromagnetic, changes into α - Fe_2O_3 at $\sim 400^\circ$. Thus, γ - Fe_2O_3 could be present in the 400° series. However, no crystalline phases of Fe_2O_3 at all were detected in preparations of this series, apparently as a result of the crystallization-preventing action of Al_2O_3 ; since Al_2O_3 itself was a crystalline phase in this series, it is probable that the dimensions of the primary particles of Fe_2O_3 were at the limit of the resolving power of the method. Considering that γ - Al_2O_3 stabilizes γ - Fe_2O_3 , as was shown in [9] and [22], and that with γ - Al_2O_3 , γ - Fe_2O_3 may survive up to 600 - 650° , while, as was shown in [23], the ferromagnetism of γ - Fe_2O_3 disappears when the linear dimensions of the crystals of this phase are less than 30 Å, it is only possible to determine whether γ - Fe_2O_3 was present in our preparations by comparing the 400 and 600° series. In actual fact, no γ - Fe_2O_3 was detected by phase analysis in any case. Moreover, preparations of the 400° series were paramagnetic, which is possible either in the absence of the γ - Fe_2O_3 phase or, as was just mentioned, with crystals less than 30 Å in size. However, in the latter case recrystallization at high temperature should lead to coarsening of the crystals of both phases and not just Al_2O_3 . Consequently, if γ - Fe_2O_3 had been present in the 400° series, it should have been detected in samples of the 600° series by x-ray methods, especially as determination of the size of Fe_2O_3 crystals showed that they were quite large (100 - 150 Å). Since γ - Fe_2O_3 was not detected in this series, we consider that this phase was absent from our ferric oxide-alumina gels. This does not agree with the literature data mentioned above on the stabilization of γ - Fe_2O_3 and the disappearance of its ferromagnetism.

However, the stabilizing action was found at low concentrations of Al_2O_3 (3 - 9%). Under coprecipitation conditions with varying concentrations of components, the possibilities of the formation of various oxide phases are determined to a considerable extent by the phase composition and structure of the starting hydroxides, as is known from work on Al_2O_3 phases. Therefore, it is possible that in our experiments, which differed substantially from those described in the literature, no γ - Fe_2O_3 was formed due to the composition of the hydroxide phases, which are isomorphous for aluminum and iron and also are undoubtedly solid solutions. As regards the crystal dimensions, if they were actually appreciably less than 30 Å, then, considering the large size of the γ - Fe_2O_3 elementary cell (8.35 Å), they could hardly be considered as a crystalline phase, as, even at 30 Å, an individual crystal could contain only 30 - 36 elementary cells and, with a decrease in the crystal size, the number should fall rapidly. In connection with unavoidable deformations of the lattice, such a phase must approach, to a large extent, the region of closest, rather than open order. In addition, it is not known whether the changes in magnetic properties of pure γ - Fe_2O_3 with the crystal dimensions are essentially the same in phases which are solid solutions, as in our case. The results we obtained show, rather, that a simple transfer of the observations of Haul and Schoon to solid solutions is not justified. The supposition that we were dealing with very small crystals of γ - Fe_2O_3 is also contradictory to the results of x-ray diffraction and magnetic investigations of the temperature section.

The paramagnetism of catalysts fired at 400° is apparently a property of the solid solution phases formed; this idea is in agreement with the results of Finch and Sincha [10], who showed that the $\alpha \rightarrow \gamma$ -Fe₂O₃ transition proceeds through the intermediate phase β -Fe₂O₃, and also with the fact that transitional complex phases are formed when oxide mixtures are heated, which was established in the work of Hüttig et al. [24]. It may be assumed that the maxima and minima in χ on the curves in Fig. 2, a are caused by precisely such transitional forms or phases which differ from each other with a change in catalyst composition (Fe₂O₃ content). It may be noted that as Fig. 2, b shows (changes in μ and Δ), this anomalous course of the changes with χ maxima is connected with a decrease in the exchange interaction between Fe³⁺ ions. This is indicated by the nature of the changes in Δ with composition.

The ferromagnetism and the maxima on the composition-susceptibility curves of catalysts of the 600 and 750° series (Fig. 3, a) are probably explained by the formation of compounds with the composition α -Al₂O₃ · β -Fe₂O₃, which have strongly ferromagnetic properties. This is confirmed by the fact that thermomagnetic curves for compounds of these compositions differ sharply from thermomagnetic curves of other samples in that they show a clear transition point. In addition, precisely these samples were reduced to the greatest extent during catalytic experiments and this is probably connected with the more ready reducibility of these intermediate compounds. The formation of such structures was demonstrated in the system CaO-Fe₂O₃ [25]. In addition, we cannot exclude the possibility of the effect of factors described in the work of Neel [26], who showed that in the Fe₂O₃ lattice there may exist small, almost two-dimensional sections of Fe₃O₄, which are so deformed that they do not differ from the α -Fe₂O₃ lattice.

This phenomenon is caused by a change in the number of Fe ions in the elementary cell. At certain concentrations of such defect sections and with their increase in size, the appearance of clearly expressed ferromagnetism could be quite a natural consequence.

Let us now consider the phase composition and properties of ferric oxide-alumina gels used in catalytic experiments. By x-ray diffraction methods it was established that the preparations of the 400° series contained Fe₃O₄, which caused their ferromagnetism. An analogous, but more weakly expressed picture was obtained for some preparations of the 600° series. No magnetite was detected in the 750° series. These data indicate that the reduction of iron oxide by hydrogen liberated during the reaction at the experimental temperatures (260-290°) proceeded through the volume in the 400° series, while the number of layers of Fe₂O₃ reduced decreased with an increase in catalyst firing temperature. For catalysts fired at 750° it may be considered as a surface effect; their ferromagnetism increased to a very small extent and the susceptibility was low. It might be considered that the reduction of Fe₂O₃ during the catalytic experiments could proceed to FeO or Fe. The ferromagnetism of the samples is evidence against the first possibility (as χ of FeO \approx 0). In addition, the appearance of FeO in Fe₂O₃ should immediately lead to the formation of Fe₃O₄ spinel, from which it follows that FeO could not have been present in the working catalysts. Reduction to metallic Fe in the system studied at such low temperatures as 260-290° is extremely improbable. For as is known from practice in the reduction of ammonia catalysts, Al₂O₃ hinders the reduction of iron to metal in them even at higher temperatures. In addition, direct experiments with Fe, FeO, Fe₂O₃, and Fe₃O₄ and isopropyl alcohol, carried out by Komarov and Burevova [27] at 300-410°, i.e., at higher temperatures than in our experiments, and also thermodynamic calculations they did, showed that the reduction of FeO to iron proceeds with much more difficulty than the formation of the phases Fe₃O₄ from Fe₂O₃ and F₂O from Fe₃O₄. In experiments with metallic iron, they showed that part of the latter was oxidized during the reaction with isopropyl alcohol. Thus, it is clear that under the comparatively brief action of i-C₃H₇OH at low temperatures, the formation of Fe₃O₄ as the sole conversion product (or as one of the conversion products) of Fe₂O₃ is quite regular.

All that has been presented shows that the results of our x-ray diffraction and magnetochemical investigations of ferric oxide-alumina gels are in good agreement and complement each other. This is extremely important from the point of view of interpreting the relation between phase composition and catalytic properties of these ferric oxide-alumina gels, which is given in the next communication.

SUMMARY

1. An investigation was made of the effect of component ratio and thermal treatment conditions on the phase composition and magnetic properties of coprecipitated ferric oxide-alumina gels containing up to 57 mol. percent of Fe₂O₃.

2. Gels fired at 400° contained only one crystalline phase, namely, a saturated solid solution of Fe_2O_3 (8 mol. %) in $\gamma\text{-Al}_2\text{O}_3$, while those fired at 600 and 750° also contained a solid solution of Al_2O_3 in $\alpha\text{-Fe}_2\text{O}_3$. No $\gamma\text{-Fe}_2\text{O}_3$ was detected either by x-ray diffraction or magnetic methods.

3. Fe_2O_3 reduced the temperature of the phase transition of $\gamma\text{-Al}_2\text{O}_3$, in which it was dissolved, to $\alpha\text{-Al}_2\text{O}_3$ and this transition occurred even at 1000°.

4. All gels fired at 400°, gels with 7 and 18 mol. % of Fe_2O_3 fired at 600°, and the gel with 8% of Fe_2O_3 fired at 750° were paramagnetic and obeyed the Curie-Weiss law with a positive value for the Weiss constant. Their paramagnetism is explained by the formation of $\beta\text{-Fe}_2\text{O}_3$ or more complex transition phases. All the other gels were ferromagnetic.

5. Catalytic reactions of isopropyl alcohol on the gels studied at 260-290° led to an increase in the ferromagnetism as a result of the formation of Fe_3O_4 .

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CATALYTIC PROPERTIES OF THE SYSTEM $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$

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The system $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ in the region of low Al_2O_3 contents has been studied in detail in connection with catalysts for ammonia synthesis. $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalysts have found application in organic catalysis and have been proposed for the dehydration of alcohols, their codehydration with ammonia and amines, and the hydrolysis of esters (their hydration to alcohols) [1-6]. Most of these catalysts had a high Al_2O_3 content. Also, it may be recalled that catalysts of the system discussed are suitable for the reaction of CO with water vapor [7-9] and that they have been studied as catalysts for CO oxidation [10]. The effect of traces of Fe_2O_3 in natural bauxites on the activity of the latter in the dehydration of alcohols has also been studied [11]. However, we were the first to make a systematic investigation in which the change in catalytic properties and structure of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ was studied in relation to the component ratio and thermal treatment conditions. This investigation is of a complex nature from the point of view of the methods used in it. The present article supplements an investigation of the adsorption properties of these catalysts [12] and a study of their phase composition and magnetic properties [13]. The overall and specific activity and the selectivity of these catalysts was determined for the decomposition of absolute isopropyl alcohol.

EXPERIMENTAL

Preparation of catalysts. The catalysts were prepared by precipitation of hydroxides with 10% ammonia from a mixture of 10% solutions of aluminum and iron nitrates in suitable ratios for giving the required catalyst compositions. The precipitation was carried out at room temperature with a final pH of 9 (determined with an LP-5 potentiometer). The precipitates were washed by decantation to remove NO_3^- , collected by filtration, and formed by passage through the die of a press. After being dried at 120° , a catalyst of a given composition was divided into three parts and each of these was fired for 7 hr at a definite temperature. In this way, we obtained three series of catalysts, fired at 400° , 600° , and 750° , respectively. The grain diameter of the catalysts was of the order of 1.1-1.3 mm. Table 1 gives the molar compositions of the catalysts from analysis data for the iron contents of the prepared samples fired at 400° . The specific surfaces of the catalysts were determined from the benzene vapor adsorption isotherms at 20° as described in [12], the phase composition and lattice constants of the phases from powder x-ray patterns, and the magnetic properties by the Faraday method; the corresponding data are given in [13].

Determination of catalytic activity. The decomposition of absolute $i\text{-C}_3\text{H}_7\text{OH}$ was carried out in a flow system at 260° , 275° , and 290° in a plug-in electric furnace, whose temperature was regulated with an ERM-237 . The reaction temperature was measured with a thermocouple in the center of the catalyst bed, the volume of which was 3 cc in all experiments. An injection burette with an SD-2 motor was used to give a steady input of alcohol at a space velocity of 1 hr^{-1} . The gaseous reaction productions were analyzed on a GIAP apparatus. The rates of the dehydrogenation and dehydration reactions were determined by the volumes of propylene (denoted by C_3H_6 in the tables) and hydrogen (H_2 in the tables), reduced to normal conditions.

TABLE 1. Volumes (in ml at s.t.p.) of C_2H_6 and H_2 Liberated during the Decomposition of 1 ml of $i-C_3H_7OH$ and the Degrees of Conversion in Percents

Catalysts	Composition in mol. %		Weight by vol. in g/cc	Specific surface in m ² /g	Temperature in °C					
	Al ₂ O ₃	Fe ₂ O ₃			260		275		290	
					C ₂ H ₆	H ₂	C ₂ H ₆	H ₂	C ₂ H ₆	H ₂
Catalysts fired at 400°	100	0	—	284	228(77)	0	289(97)	0	—	—
	92	8	0,76	363	55(20)	0	166(56)	0	265(89)	0
	82	18	0,83	350	42(14)	2(0,7)	129(43)	7(2)	212(71)	12(4)
	68	32	0,80	320	46(16)	6(2)	134(46)	17(6)	216(73)	26(9)
	60	40	0,86	276	50(17)	14(5)	137(47)	38(13)	207(70)	43(15)
	54	46	0,96	267	59(19)	15(5)	160(55)	35(12)	196(67)	36(12)
	43	57	1,00	263	46(15)	22(7)	113(38)	56(19)	154(52)	59(20)
Catalysts fired at 600°	92	8	0,73	215	135(45)	0	227(78)	0	272(92)	0
	82	18	0,86	203	77(26)	4(1)	195(67)	6(2)	273(92)	7(2)
	68	32	0,80	160	136(46)	4(1)	181(62)	5(2)	275(93)	4(1)
	60	40	0,90	146	104(35)	8(3)	191(64)	9(3)	271(91)	11(4)
	54	46	1,00	125	87(30)	9(3)	160(54)	14(5)	252(85)	13(5)
	43	57	1,0	122	81(27)	13(4)	128(43)	20(7)	183(63)	37(12)
	Catalysts fired at 750°	100	0	—	135	256(86)	0	286(97)	0	—
92		8	0,73	149	80(27)	0	146(50)	0	263(89)	0
82		18	0,83	122	56(20)	3(1)	139(47)	6(2)	251(85)	6(2)
68		32	0,80	81	33(11)	2(1)	107(36)	6(2)	217(73)	12(4)
60		40	0,90	76	82(27)	3(1)	134(45)	6(2)	196(66)	9(3)
54		46	1,00	58	35(12)	4(1)	105(36)	11(4)	190(64)	16(5)
43		57	1,03	63	44(15)	10(3)	81(27)	25(8)	105(35)	29(10)

Table 1 gives the volumes of gases liberated during the decomposition of 1 ml of alcohol and the degrees of conversion are given in brackets. In most cases repeat experiments at 260° after the main series gave results which differed little from those of the first experiments at 260°, indicating that the state of the catalyst did not change during experiments. Gaseous reaction products were liberated steadily during the experiments. The rate constants of the reactions were calculated from the approximate equation for monomolecular reactions in the flow system, $k = \frac{N \cdot m}{M - m/2}$, which was proposed by Balandin and Bork [14]. The data obtained are given in Table 2, in which three figures are given in each square; these are the values of k for experiments with catalysts fired at 400° (top line), 600° (middle line), and 750° (bottom line). Table 2 shows that in all cases, even with a predominance of ferric oxide in the catalysts, k for dehydration considerably exceeded k for dehydrogenation (subsequently denoted by k').

EXPERIMENTAL RESULTS

An examination of the data on the degrees of conversion given in Table 1 shows that the over-all dehydrating activity of the catalysts was lower than for Al_2O_3 and decreased with an increase in their Fe_2O_3 content, despite the fact that some of the mixed catalysts had a higher specific surface, S , than Al_2O_3 obtained under analogous conditions. Dehydrogenation of alcohol became measurable on catalysts with more than 8-10 mol. % of Fe_2O_3 and increased with an increase in the iron concentration. Both of these relations were found at all three catalyst firing temperatures. The following was observed for the corresponding change in the dehydration rate constants: A change from pure Al_2O_3 to mixed catalysts was accompanied by a considerable fall in the value of k . After this, k successively decreased with an increase in the Fe_2O_3 content of the catalysts in all cases, except for catalysts fired at 400°, where k was small and hardly changed with a change in the Fe_2O_3 content. On the other hand, k' increased in all cases with an increase in the Fe_2O_3 content of the catalysts. We used the values of k and k' for calculating the specific activity A_{sp} and the selectivity coefficient K_s of the catalysts.

Specific activity and phase composition of catalysts. The specific activity was expressed in the form proposed by Borekov [15]: $A_{sp} = k/S$, where k is the rate constant of the reaction and S the specific surface in m^2/g . Below, A_{sp} is used for dehydration and A'_{sp} for dehydrogenation. For convenience, the values of k/S are multiplied by 10^4 . The change in A_{sp} with composition and firing temperature is shown in Fig. 1 and the analogous picture for A'_{sp} in Fig. 2. An examination of these figures clearly shows that A_{sp} and A'_{sp} increased with an increase in the alcohol decomposition temperature within the limits of each series (400, 600, and 750°) of catalysts.

TABLE 2. Rate Constants of Dehydration and Dehydrogenation of i-C₃H₇OH on Al₂O₃-Fe₂O₃ Catalysts

Al ₂ O ₃ content in mol. %	k _{260°}		k _{275°}		k _{290°}	
	C ₃ H ₆	H ₂	C ₃ H ₆	H ₂	C ₃ H ₆	H ₂
100	0,083	0	0,128	0	—	—
	0,101	0	0,124	0	—	—
92	0,0136	0	0,051	0	0,106	0
	0,039	0	0,083	0	0,112	0
	0,020	0	0,043	0	0,106	0
82	0,010	0,0005	0,037	0,002	0,074	0,004
	0,020	0,0010	0,064	0,0019	0,112	0,003
	0,014	0,0006	0,041	0,002	0,097	0,002
68	0,011	0,0015	0,039	0,005	0,075	0,009
	0,040	0,0013	0,058	0,002	0,115	0,002
	0,076	0,0005	0,029	0,002	0,078	0,004
60	0,011	0,003	0,040	0,001	0,071	0,014
	0,027	0,002	0,062	0,003	0,111	0,004
	0,020	0,0009	0,040	0,0016	0,065	0,003
54	0,012	0,003	0,049	0,010	0,065	0,012
	0,023	0,0025	0,049	0,004	0,098	0,006
	0,009	0,0009	0,027	0,003	0,062	0,005
43	0,011	0,005	0,032	0,016	0,051	0,020
	0,020	0,003	0,036	0,006	0,061	0,012
	0,011	0,003	0,020	0,006	0,028	0,007

The firing temperature of the catalysts also had an effect, and A_{sp} and A'_{sp} increased with an increase in the firing temperature, though there were individual cases where higher values were obtained at 600° than at 750°. Since this did not occur at all alcohol decomposition temperatures, for example, only at 260° for catalysts with 8 and 46 mol. % of Fe₂O₃, it can be assumed that these few deviations from the general pattern were the result of certain errors in the measurement of S or the reaction rates. The magnitude of these deviations was small and therefore they hardly deserve more detailed discussion.

The first noteworthy fact about Fig. 1 is that A_{sp} for all the mixed catalysts was much lower than the activity of pure γ -Al₂O₃ obtained by the same method and under analogous conditions. It should be noted that no experiments were carried out with Al₂O₃ at 290°, as a very high degree of conversion, (of the order of 97%) was reached even at 275° and a further rise in experimental temperature was pointless. Thus, the experiments showed that both the over-all and specific dehydration activity decreased with the introduction of Fe₂O₃ into the catalyst, i.e., with a change from Al₂O₃ to mixed catalysts. The reasons for this become clear on examining the phase composition, the determination of which was described in [13]. It was found that Fe₂O₃ in the catalysts was partly present in the form of a solid solution in γ -Al₂O₃ with a saturated solution formed at 8 mol. % of Fe₂O₃, while at higher concentrations of Fe₂O₃ in the catalysts, the excess formed a phase which was a solid solution of Al₂O₃ in it. The formation of a solid solution of Fe₂O₃ in Al₂O₃ was accompanied by an increase in the parameter of the Al₂O₃ crystal lattice. The sharp change in activity when Fe₂O₃ was introduced into Al₂O₃ was the result of the formation of the solid solution, i.e., the change in the chemical nature of the dehydrating component (and phase) of the catalyst and the accompanying changes in the electronic state and lattice parameters. Since a saturated solution is formed when only 8 mol. % of ferric oxide is dissolved in Al₂O₃, with an increase in the Fe₂O₃ content, the dehydrating activity should remain lower than for Al₂O₃, but constant. However, as the curves in Fig. 1 show, this does not occur. Even for catalysts fired at 400°, for which the change in A_{sp} is close to linear, the activity changes with composition more noticeably, the higher the alcohol decomposition temperature. Firing the catalysts at 600 and

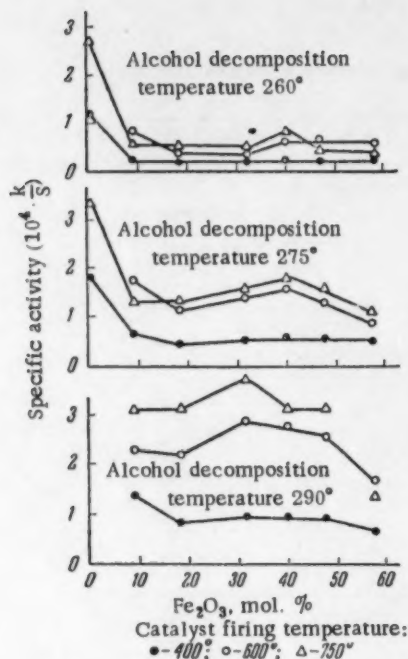


Fig. 1. Relation between specific activity (dehydration) and composition of catalysts.

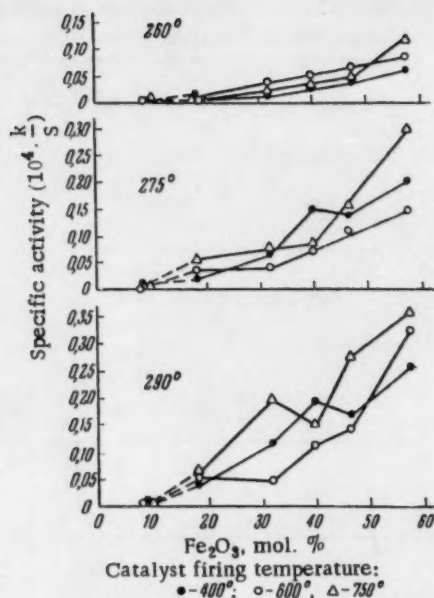


Fig. 2. Relation between specific activity (dehydrogenation) and composition of catalysts.

750° led to large changes in A_{sp} and the appearance of maxima at 30-40 mol. % of Fe_2O_3 . We consider that the changes in dehydrating activity with catalyst composition may be explained by localization of the most active centers of the catalyst surface at the grain boundaries (as was previously demonstrated experimentally in [16, 17]). In this case, an increase in the Fe_2O_3 concentration up to a certain limit should lead to an increase in the interphase surface and then, after a certain concentration is reached, the relative proportion of interphase surface should decrease with an increase in the Fe_2O_3 content.

Localization of the most active sections of the surface on the interphase boundary must be connected with diffusion phenomena in solids. Interpenetration in the surface layers of these phases must lead to local metastable formations on the surface and to a sharp change in its electronic properties, i.e., to a change in the reactivity of the surface. It is also possible that at the phase boundary, the desorption of reaction products is facilitated by the action of the second phase and the acceleration of the reaction is a result of this factor.

Continuing the comparison of results illustrating the effect of thermal treatment on the catalyst properties, it should be noted that catalysts fired at 400° were very highly disperse and had a comparatively weakly expressed crystal structure, as was shown by x-ray diffraction [13]. An increase in firing temperature led to greater crystallinity, and consequently to a higher specific activity, as is shown by Fig. 1. The increase in specific surface was not involved in this as A_{sp} was expressed as the activity per m^2 of surface. Analysis of the pore structure of catalysts [12] showed that the mean pore diameter increased appreciably with a rise in firing temperature, corresponding to the growth of crystals in the catalyst, which affected the values of A_{sp} to a greater extent over the temperature range 400-600° than over the range 600-750°. Apparently, firing at 600° was sufficient to yield a porous structure, making the whole surface of the catalyst accessible to reagent molecules. It may be added that the most active of the mixed catalysts were samples with 32-40 mol. % of Fe_2O_3 , which were found to be most heterogeneous with respect to pores.

As has already been mentioned above, catalysts containing less than 18 mol. % of Fe_2O_3 did not dehydrogenate alcohol at all over the temperature range investigated: $A'_{sp} = 0$. At 18 mol. % Fe_2O_3 , A'_{sp} was small, but increased rapidly and nonlinearly with an increase in the Fe_2O_3 content and also with a rise in decomposition temperature, as is clearly shown by Fig. 2. Special experiments with pure Fe_2O_3 prepared under analogous conditions

showed that at 290° it mainly dehydrogenated isopropyl alcohol (H_2 90%, C_3H_6 10%). Therefore, an increase in the Fe_2O_3 concentration from 9 mol. %, when it still did not form a separate phase, to 18%, when it was already present as a separate phase, naturally produced a change in the selectivity of the catalyst and partial dehydrogenation of the alcohol. The increase in dehydrogenation with a further increase in Fe_2O_3 content is primarily explained by the concentration factor. However, it should also be remembered that x-ray structural analysis showed [13] that the Fe_2O_3 phase was not pure, but consisted of a solid solution of Al_2O_3 in Fe_2O_3 in which the Al_2O_3 content could reach 25%. The formation of such a solid solution in the catalysts studied was facilitated by the fact that they were obtained by coprecipitation. From the rapid increase in A'_{sp} with an increase in Fe_2O_3 concentration in the catalysts, it follows that a solid solution of Al_2O_3 in Fe_2O_3 has quite a high dehydrogenating activity. However, this activity is obviously less than that of Fe_2O_3 itself as $A'_{sp} \gg A_{sp}$ even when the catalyst contained 60 mol. % of Fe_2O_3 and the phase of the $Fe_2O_3-Al_2O_3$ solid solution predominated. This occurred at all experimental temperatures.

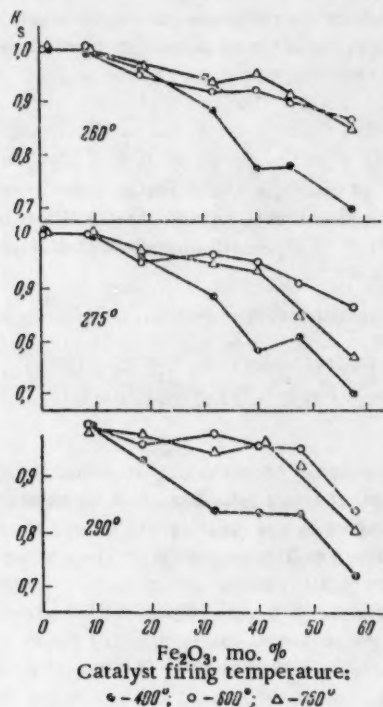


Fig. 3. Relation between specificity coefficient and composition.

Selectivity of catalysts. Figure 3 shows data on the change in selectivity of catalysts with composition and firing temperature. The specificity coefficient K_s was expressed in the form of the ratio $A'_{sp}/A_{sp} + A'_{sp}$. The greatest range of changes in K_s with composition was observed for catalysts fired at 400° and this was the case at all temperatures for the catalytic experiments. For catalysts fired at 600 and 750°, considerable changes in K_s occurred in the region of Fe_2O_3 concentrations from 40 to 60 mol. %, while in the range from 0 to 40 mol. %, K_s did not change much, and in the region of 18-40 mol. %, there was a section with practically constant values of K_s for a given firing temperature. Thus, the changes in K_s with composition are in good agreement with the ideas given above on the effect of phase composition on activity, since, in the region where there is a saturated solution of Fe_2O_3 in Al_2O_3 , K_s changes little, while in the region where the concentration of the second phase becomes large or even predominant, K_s decreases considerably more rapidly, which, in the expression adopted for K_s , corresponds to an increase in dehydrogenation.

Comparison with results of magnetic measurements. Magnetochemical investigation [13] showed the essential differences between the series of catalysts fired at 400° and those fired at 600 and 750°. All catalysts of the 400° series were found to be paramagnetic, while those with 18 mol. % and more of Fe_2O_3 from the 600 and 750° series showed ferromagnetism, i.e., their magnetic susceptibility depended on the field strength. Since Al_2O_3 itself is diamagnetic, the paramagnetism of the 400° series is determined by the solution of Fe_2O_3 in Al_2O_3 .

By comparing the curves for the change in dehydrogenating activity A'_{sp} with composition, on the one hand, with the curve for the change in magnetic susceptibility per g of catalyst χ with composition, on the other hand (Fig. 4), it is possible to see that they are sybatic; in this paramagnetic series of catalysts, the dehydrogenating activity changes with composition in the same way that the magnetic susceptibility changes. It should be emphasized that for catalysts of the 400° series that had been used, the magnetic susceptibility increased strongly in comparison with the original state and clearly expressed ferromagnetism appeared and increased with an increase in the Fe_2O_3 concentration. It apparently appeared as a result of reduction of part of the Fe_2O_3 to Fe_3O_4 . However, this does not alter the essential point: Both the paramagnetic susceptibility of catalysts of this series before operation and their ferromagnetism after catalytic experiments increase with the Fe_2O_3 concentration, though by different laws. Even if it is assumed that the ferromagnetic phase Fe_3O_4 is responsible for dehydrogenation of the alcohol, attention must be paid to the fact that it is gradually formed from the paramagnetic phase, and, consequently, the parallelism between the changes in A'_{sp} and χ noted is still valid. However, from the considerations and facts

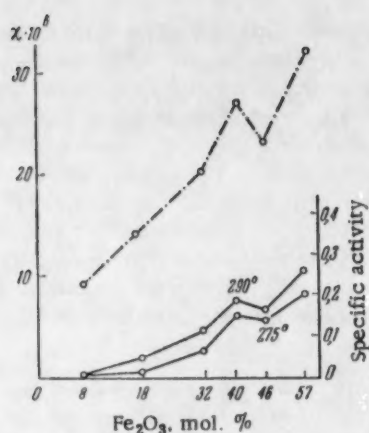


Fig. 4. Change in specific activity (dehydrogenation) and magnetic permeability in relation to the composition of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalysts fired at 400° .

activity in dehydrogenation with data on the magnetic susceptibility of catalysts after the reaction throws light on the ratio of the activities of the paramagnetic and ferromagnetic phases.

The ferromagnetism of used catalysts increased differently in relation to firing temperature; it increased to the greatest extent for catalysts fired at 400° as is shown by Table 3, which gives values of the susceptibility χ per g of catalyst. In certain cases (for example, at 57 mol. % of Fe_2O_3) χ_{400} exceeds χ_{600} by a factor of 20 and χ_{750} by a factor of 300. The general picture is that χ_{400} is much greater than χ_{600} and many times greater than χ_{750} for corresponding concentrations of Fe_2O_3 .

TABLE 3. Magnetic Susceptibility of Used Catalysts

Fe_2O_3 content in mol. %	$\chi \cdot 10^6$ for catalysts fired at		
	400°	600°	750°
18	1 800	1 250	250
32	7 000	950	67
40	13 000	420	67
46	17 500	5 500	164
57	20 400	1 000	73

of the 400° series. At 275 and 290° the picture is more complex, but, with the exception of the catalyst with 40 mol. % of Fe_2O_3 , all catalysts of the 750° series were less ferromagnetic and much more active than corresponding catalysts of the 400° series. Some catalysts of the 600° series were more, and some less active than the corresponding catalysts of the 400° series, while some were less active than corresponding catalysts of the 750° series. From the fact that Fe_3O_4 in the catalysts is only formed as a result of reaction of Fe_2O_3 with alcohol or H_2 , liberated during dehydrogenation, it follows that this phase must be localized in the surface layers of the catalyst grains and that there cannot be essential differences in the distribution of this phase in catalysts of all three series.

All that has been presented above shows that the dehydrogenation of $i\text{-C}_3\text{H}_7\text{OH}$ occurs mainly on the paramagnetic phase, i.e., the solid solution of Al_2O_3 in Fe_2O_3 . If the activity of the ferromagnetic phase even slightly exceeded that of the $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ solid solution, this would affect the results of the reaction, even with low

presented below, it follows that the assumption that the dehydrogenation of alcohol occurs solely or predominantly on the ferromagnetic phase is not justified.

As has already been mentioned, catalysts with more than 18 mol. % of Fe_2O_3 fired at 600 and 750° were ferromagnetic. However, their ferromagnetism was very weak and corresponded to extremely low concentrations of ferromagnetic phase in the catalysts. From comparison with the Fe_2O_3 content of the catalysts it follows that a very large part of the Fe_2O_3 in catalysts of the 600 and 750° series also was a paramagnetic solid solution of Al_2O_3 in $\alpha\text{-Fe}_2\text{O}_3$, which was also confirmed by x-ray structural analysis. Since the catalysts were not reduced before operation and Fe_3O_4 could not be formed in them, their ferromagnetism could only be caused by the presence of small amounts of $\gamma\text{-Fe}_2\text{O}_3$. Thus, a certain time after the beginning of alcohol decomposition, the catalysts contained three phases: a paramagnetic solution of Al_2O_3 in $\alpha\text{-Fe}_2\text{O}_3$ and ferromagnetic Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, possibly with Al_2O_3 dissolved in each of them. A comparison of data on specific

Thus, the concentration of the ferromagnetic phase must be greatest in used catalysts of the 400° series and this is readily explained by the great ease of reduction of Fe_2O_3 to Fe_3O_4 in samples fired at the lower temperature due to their greater specific surface in comparison with corresponding catalysts of the 600 and 750° series. Consequently, if the ferromagnetic phases, i.e., in the first instance Fe_3O_4 and then $\gamma\text{-Fe}_2\text{O}_3$, were responsible for the dehydrogenation of alcohol, then catalysts of the 400° series should have the greatest activity. An examination of the data in Tables 1 and 2 and Fig. 2, shows that this is not actually the case and that there is no direct relation between the ferromagnetism of the catalysts and their dehydrogenating activity. Actually, all catalysts of the 600 and 750° series were more active at 260° than the corresponding catalysts

concentrations of Fe_3O_4 in the form of some proportionality between the change in activity and the amount of ferromagnetism. From the absence of this relation we can conclude that either the activities of the solid solution and Fe_3O_4 are equal or, as is more probable, the $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ solid solution is more active.

We have not discussed the possibilities of the presence of metallic iron in the used catalysts as it was not detected by phase analysis. However, the negative result of x-ray diffraction analysis does not exclude the possibility of metallic iron on the surface, which we considered improbable for a number of reasons. The work of Komarov and Burevova [18] appeared quite recently, and, by direct experiments on the decomposition of $i\text{-C}_3\text{H}_7\text{OH}$ on metallic iron, the authors showed by analytical and micrographic methods that the iron was partly oxidized, and its surface consisted of ferrous oxide after experiments. Thus, the considerations presented above on phase composition and dehydrogenating activity were again confirmed.

SUMMARY

1. An investigation was made of the effect of composition and thermal treatment conditions of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalysts on the specific activity in the dehydration (A_{sp}) and dehydrogenation (A'_{sp}) of $i\text{-C}_3\text{H}_7\text{OH}$ at 260-290°.
2. Dehydration of alcohol occurs on the Al_2O_3 phase with Fe_2O_3 dissolved in it. The addition of Fe_2O_3 strongly reduces A_{sp} of Al_2O_3 , though it also passes through a maximum at 32-40 mol. % of Fe_2O_3 . With a rise in catalyst firing temperature from 400 to 750°, A_{sp} increases.
3. Dehydrogenation, which is caused by the solid solution of Al_2O_3 in Fe_2O_3 , becomes appreciable with an Fe_2O_3 content of 18 mol. %; A'_{sp} increases rapidly and nonlinearly with an increase in Fe_2O_3 concentration and a rise in catalyst firing temperature.
4. A'_{sp} for catalysts fired at 400° (all paramagnetic) changes with composition symbatically with the value of the magnetic susceptibility. No relation was observed between the ferromagnetism of catalysts and A'_{sp} .
5. Although some $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalysts have a considerably greater specific surface, their over-all dehydrating activity is lower than that of Al_2O_3 obtained under analogous conditions.

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VAPOR-PHASE HYDRATION OF PROPYLENE OXIDE OVER TRICALCIUM PHOSPHATE

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Tricalcium phosphate is an active stable and specific catalyst for hydrolysis, hydration, and dehydration. It was recently established that it also catalyzes the hydrolytic cleavage of mesityl oxide to acetone [1] and cyclohexylidenecyclohexanone-2 to cyclohexanone [2]. It may be conjectured that the activity of the phosphate in processes of an acid-base nature may be caused by its weakly acidic properties [3].

The catalytic properties of calcium phosphate in the hydration of propylene oxide were studied in the present work. A review of work on the hydration of organic oxides was given in the monograph of Curme and Johnston [4]. Ethylene oxide does not react with water vapor, even at 200° [5], but in the presence of the catalysts H^+ and OH^- ions it is hydrated even at room temperature. For industrial purposes ethylene oxide is hydrated in the liquid phase in the presence of mineral acids (for example, 0.5% sulfuric acid) at 50-70°. The glycol yield exceeds 90% of theoretical [4]. The reaction may also be carried out in the absence of catalysts in the liquid phase at 180-200° under pressure. A large excess of water (12-20-fold) is used to prevent the formation of polyglycols both in the presence of catalyst and without it. The latter circumstance, which involves a considerable consumption of heat in the isolation of the product, and also the difficulties arising during the additional, careful freeing of the reaction products from traces of acid, compels a search for new methods of carrying out this process. In particular, heterogeneous vapor-phase hydration is apparently a promising method. Little study has been devoted to the hydration of oxides on solid catalysts. The main difficulty in achieving the vapor-phase hydration of oxides is their tendency to isomerize into the corresponding aldehydes or ketones. In the hydration of ethylene oxide on silica gel, phosphoric acid on silica gel, or aluminum or thorium oxide over the temperature range of 153-167° with a molar ratio of water to oxide of 2 to 19, a water-aldehyde mixture was obtained and glycol was not detected in the reaction products [6]. Only silver oxide (8.7%) deposited on aluminum oxide catalyzed the hydration. At 150-210° the ethylene oxide conversion in one pass was 20-30%. After the catalyst had operated for 5-6 hr, its activity fell sharply due to blocking of its surface with tarry products. The catalyst did not recover its activity completely after treatment with superheated steam. Ion-exchange resins, both acid and basic, have been recommended as catalysts for ethylene oxide hydration. At 115°, a slight pressure, and a molar ratio of water : ethylene oxide of 10:1, the glycol yield was 80-85% [7].

The results of our work show that tricalcium phosphate is an active and selective catalyst for the hydration of oxides in the vapor phase.

EXPERIMENTAL

The experiments were carried out on the flow apparatus described previously [1]. The temperature in the catalyst bed was maintained with an accuracy of $\pm 1^\circ$. Into a Pyrex tube was placed 20 ml of calcium phosphate in the form of granules, 2 x 3 mm, obtained from calcium chloride and diammonium phosphate. After each experiment, the catalyst was regenerated with air for 2 hr at 400-450°. Propylene oxide and water in definite ratios were passed at a steady rate over the catalyst with the aid of an automatic doser and cut-out [8]. The injector of the doser from which the propylene oxide was introduced was cooled with ice. The ethylene oxide flow rate was determined with a rheometer.

Analysis of reaction products. In each experiment, 8.5 ml (7.1 g) of propylene oxide was normally passed through the catalyst. The reaction products were fractionated on a column with an efficiency of 20 theoretical plates. The unreacted oxide distilled at 33-35°. Then a broad fraction was collected at 45-90° and this probably contained allyl alcohol and propionaldehyde. For example, in an experiment at 232° with a molar ratio of water : propylene oxide of 12:1 and a contact time of 15.7 sec, we obtained 0.7 g of this fraction and the oxime method showed that it contained 11.6% of carbonyl-containing compound, calculated on propionaldehyde. Hydrogenation in the presence of Raney nickel catalyst at 20° showed that it contained 35.2% of unsaturated compound, calculated on allyl alcohol.

At 100° we collected a certain amount of pure water. A water-glycol mixture, containing 10-15% of glycols, remained in the still boiler. In separate experiments, when a sufficient amount of aqueous glycol solution had accumulated, it was distilled with the isolation of glycol. The glycol content of the aqueous solution was determined from the refractive index [4] as the catalyzate consisted only of water and glycols and the amount of di- and polyglycols did not exceed 15-20% of the total amount of glycols. In control experiments, satisfactory agreement was found between the amounts of propylene glycol isolated by fractionation and the amounts determined refractometrically.

The propylene oxide used in the experiments was first distilled over metallic sodium and had b.p. 34.0-34.5° (760 mm); n_D^{20} 1.3657; d_4^{20} 0.8306. Commercial ethylene oxide was used.

Effect of temperature, contact time, and the water : propylene oxide ratio. The effect of temperature on the degree of conversion of propylene oxide is shown in experiments 1-12 (table) and Fig. 1. The data presented show that over the temperature range 130-194° (experiments 1-5) the glycol yield changed little. No by-products were present. When the temperature was raised to 260°, the glycol yield began to increase rapidly and at 232° it was 28% and at 260°, 40%. The formation of by-products forming the fraction with b.p. 45-90° simultaneously became appreciable. With a decrease in the contact time (experiments 9 and 10) in the temperature range 190-230°, the glycol yield also changed little (from 9 to 14%), while in the temperature range 230-260°, it increased to 27%. With a further increase in temperature to 280°, the glycol yield changed insignificantly, but at the same time, up to 20% of by-products was formed.

Effect of Temperature, Contact Time, and Water : Propylene Oxide Ratio on the Propylene Glycol Yield

Expt. No.	Temp. °C	Contact time, sec	H ₂ O : C ₃ H ₆ O molar ratio	C ₃ H ₈ O ₂ yield on oxide passed, %	Expt. No.	Temp. °C	Contact time, sec	H ₂ O : C ₃ H ₆ O molar ratio	C ₃ H ₈ O ₂ yield on oxide passed, %
1	134	9,4	6,8 : 1	11	11	260	4,7	6,8 : 1	27
2	153	9,4	6,8 : 1	14	12	280	4,7	6,8 : 1	27
3	163	9,4	6,8 : 1	13	13	232	3,1	6,8 : 1	11
4	184	9,4	6,8 : 1	15	14	232	4,7	6,8 : 1	14
5	194	9,4	6,8 : 1	14	15	232	9,4	6,8 : 1	28
6	232	9,4	6,8 : 1	28	16	232	14,0	6,8 : 1	48
7	240	9,4	6,8 : 1	31	17	260	4,7	3,3 : 1	21
8	260	9,4	6,8 : 1	40	18	260	4,7	6,8 : 1	28
9	193	4,7	6,8 : 1	9	19	260	4,7	13,2 : 1	38
10	232	4,7	6,8 : 1	14	20	260	4,7	19,7 : 1	50

The effect of contact times between 3.1 and 14.0 sec was studied. Experiments 13-16 and Fig. 2 show that at 232° and a molar ratio of water to propylene oxide of 6.8 : 1, an almost linear relation was observed between the glycol yield and the contact time. At a contact time of 14.0 sec, the degree of conversion of oxide into glycol was 48%. However, with an increase in contact time, there was an increase in the formation of by-products and a decrease in the glycol yield on the oxide reacting.

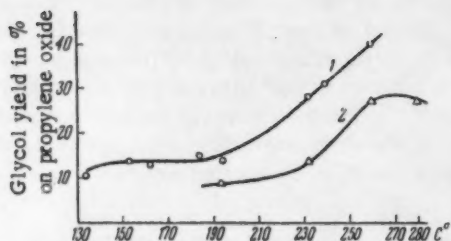


Fig. 1. Effect of temperature on propylene glycol yield at contact times of 9.4 sec (1) and 4.7 sec (2).

Experiments 17-20 and Fig. 3 show that there is a linear relation between the propylene glycol yield and the molar ratio of water : propylene oxide. At 260°, a contact time of 4.7 sec, and a molar ratio of water : oxide of 19.7 : 1, the glycol yield reached 50%. In experiments 18-20 the glycol yield on the propylene oxide reacting was 90-93%. It is important that in the presence of a large excess of water not only did the glycol yield increase, but there was also a decrease in the formation of by-products (fraction with b.p. 45-90°).

Study of catalyst stability. Two long experiments were carried out to determine the stability of the catalyst in the process investigated. The water-glycol mixtures collected were distilled with the isolation of pure propylene glycol.

Experiment 21. Water and propylene oxide in a ratio of 6.4 : 1 were passed through 20 ml of catalyst at 232° with a contact time of 4.7 sec. A total of 115 ml of propylene oxide was passed. Over a period of 18 hrs operation without regeneration of the catalyst, there were no appreciable changes in the activity of the catalyst and the propylene glycol yield, determined every 2 hr, varied over the range 12.5-15.5%.

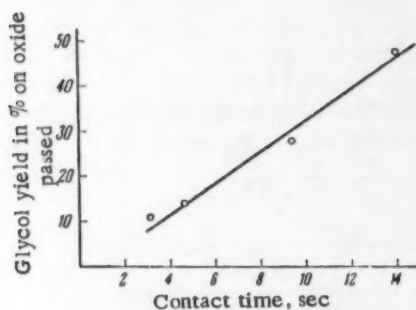


Fig. 2. Effect of contact time on propylene glycol yield.

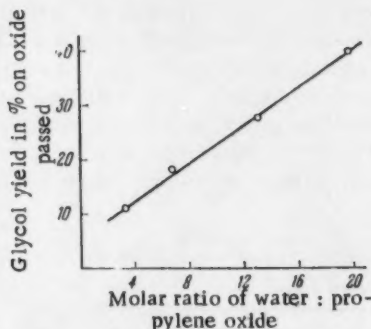


Fig. 3. Effect of the molar ratio of water : propylene oxide on propylene glycol yield.

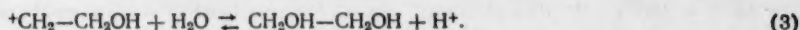
Experiment 22. In 14 hours operation without regeneration, 42.5 ml of propylene oxide was passed over 60 ml of catalyst at 232° with a contact time of 9.4 sec and a molar ratio of water : propylene oxide of 19.7 : 1. Control analyses were carried out after every 2 hr. The propylene glycol yield was 50-57%.

When a mixture of oxide, water, and glycol was passed under analogous conditions, the catalyst activity fell rapidly, but was recovered after regeneration. When the products collected in experiments 21 and 22 were distilled at 10 mm, two fractions were collected: Fraction I, with b.p. 80-83°, consisted mainly of propylene glycol, and fraction II, with b.p. 90-108°, was mainly dipropylene glycol. In experiment 21, di- and polyglycols formed 15% of the total amount of glycol, and, in experiment 22, 17%. Approximately 5% of low-boiling products (45-90°) was formed in the latter experiment.

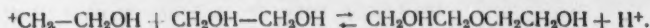
Hydration of ethylene oxide. Experiments were also carried out on the hydration of ethylene oxide. The ethylene glycol content of the catalyzates was determined refractometrically. At 232°, a molar ratio of water : ethylene oxide of 12.4 : 1, and a contact time of 10.1 sec, the ethylene glycol yield was 37.0%. The acetaldehyde yield represented 1.6-1.7% on the oxide passed.

EXPERIMENTAL RESULTS

It was established in [9] that the hydration of ethylene oxide in the liquid phase, catalyzed by H^+ ions, proceeds by the mechanism



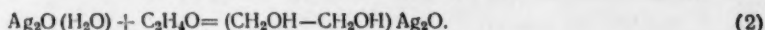
Stage (2) is the slowest. The formation of polyglycols also proceeds through the oxonium complex:



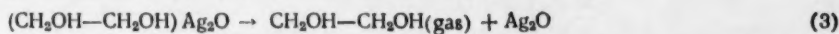
It is probable that vapor-phase hydration of ethylene oxide catalyzed by ion-exchange resins also proceeds by the same mechanism [10]. A completely different mechanism was proposed for vapor-phase hydration of ethylene oxide on a solid catalyst, silver oxide on aluminum oxide [6]. The catalytic action of the silver oxide was explained by activation of the water molecule:



The complex formed reacts with an unactivated oxide molecule:



Then follows the slowest stage of the process, namely, desorption of the glycol formed



and regeneration of the catalyst. However, if activation of the organic component of the reaction on this catalyst is not obligatory, then the route by which aldehyde is formed in the process remains incomprehensible.

The data obtained in our work indicate that hydration of oxides in the presence of calcium phosphate proceeds by the same mechanism as in the liquid phase in the presence of H^+ ions. This is confirmed by the linear relation of glycol yield to contact time and is in accord with the behavior of the phosphate catalyst in other hydrolysis and hydration processes.

In the vapor-phase hydration of oxides on solid catalysts there are a number of peculiarities, which are connected with the different adsorbabilities of water, the starting oxide, and the glycols formed. In particular, this may explain the slow increase in the yield of glycol on calcium phosphate with a rise in temperature over a definite range and also the direct relation between the glycol yield and the water excess. It is probable that a rise in temperature and an increase in the water excess accelerate the desorption of glycols blocking the catalyst surface. The high specificity of calcium phosphate in hydration reactions gives grounds for assuming that isomerization of the oxide, which proceeds readily on other catalysts, is hindered on this catalyst. The experiments confirmed this. Thus, when propylene oxide was passed over the catalyst in the absence of water at 210° with a contact time of 7 sec, less than 1% of allyl alcohol and propionaldehyde was formed and at 280° , 8%. Allyl alcohol was completely unchanged on this catalyst at 230° and only 4% was isomerized to aldehyde at 320° .

It seemed interesting to compare the results of the present work with those obtained on other catalysts under similar temperature conditions. When a basic catalyst, namely, lithium phosphate, was used, propylene oxide was readily isomerized to allyl alcohol and propionaldehyde in the absence of water [11]. In experiments with phosphoric acid on silica gel, ethylene oxide only underwent isomerization and was not hydrated. Hydration proceeded selectively in the presence of sulfuric acid, silver oxide, ion-exchange resin, and calcium phosphate. The phosphate catalyst was better than the silver oxide in selectivity, stability, and regeneration. The stability and specificity of the phosphate catalyst may make it possible to use it in practice. In this case, it would be advantageous to use a continuous process with condensation of the high-boiling glycol and return of the unreacted oxide and water vapor to the reaction.

SUMMARY

1. The catalytic activity of tricalcium phosphate in the vapor-phase hydration of propylene oxide to propylene glycol was studied.
2. Calcium phosphate is a stable and selective catalyst for this reaction.
3. The effect of temperature, contact time, and water excess on the glycol yield was studied. Considerable amounts of glycol were formed under the optimal conditions and the glycol yield reached 50-57% at 232°, for example similar results were obtained in the hydration of ethylene oxide.
4. The high specificity of the phosphate catalyst in the hydration of propylene oxide is in accord with the fact that it hardly catalyzes the isomerization of oxide to allyl alcohol and propionaldehyde.
5. The reaction mechanism is discussed.

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EFFECT OF INTERACTION AND HETEROGENEITY IN THE ACTIVE SURFACE ON THE LAWS OF CHEMISORPTION ON NICKEL

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Quantum-mechanical calculation of the interaction of a metal with a free molecule, solved as a multielectron problem, gave an unexpected result. Due to the high value of the screening charge of an adsorbed molecule on metallic catalysts in contrast to semiconductor catalysts, there should be no changes in the heats and activation energies of adsorption due to the effect of the interaction. According to a calculation carried out by Bonch-Bruevich and Glasko [1], the Langmuir equation should be obeyed on metallic catalysts with a homogeneous surface right up to high degrees of covering of the surface. The laws of chemical adsorption and catalysis observed experimentally on metallic catalysts do not differ from those observed for oxide and other catalysts. In an overwhelming majority of investigations, there are relations of a non-Langmuir type, which many authors ascribe to the effect of a change in the work function and other factors, which is arbitrarily called the "interaction" of adsorbed molecules [2, 3]. De Boer [4] considers that the main reason for the changes in heats and activation energies of adsorption on metals is a change in the work function of electrons due to the formation of a charged layer of adsorbed molecules. Due to the prevalence of ideas on the paramount role of the effect of interaction on the laws of chemisorption, it seemed interesting to study this problem experimentally.

The existence of isotopic tracer methods makes it possible to assess the degree of effect of heterogeneity and interaction on the laws of chemisorption. An investigation of the kinetic laws of the exchange of adsorbed labeled gas with gas differing in isotopic composition makes it possible to examine quantitatively the effect of heterogeneity under conditions that exclude the effect of interaction [5]. The application of statistical analysis to the investigation of kinetic laws of exchange makes it possible to obtain more reliable data on heterogeneity of the active surface with respect to activation energies of the exchange process [6]. With any exchange mechanism, the activation energies of this process are related to the heats of adsorption. The "desorption isotopic method" for investigating interaction, by the authors, which was proposed makes it possible to study the effect of interaction on chemisorption, independent of heterogeneity of the active surface [7]. By applying these methods, it is possible to obtain the required information on the extent of the effect of heterogeneity and "interaction" on chemisorption.

EXPERIMENTAL

Two types of nickel catalyst, prepared by different methods, were investigated: Sample 1 was prepared by reduction of granulated nickelous oxide in a stream of hydrogen at 300° for 20 hr. Before an experiment, the sample was reduced again with hydrogen in a reactor at 500° and then outgassed by evacuation to 10^{-6} mm at the same temperature. The specific surface, found by measuring the equilibrium adsorption of benzene, equaled 12 ± 1.5 m²/g. X-ray structural analysis showed that metallic nickel was obtained under these conditions and no oxide phase was present. Sample 2 was prepared by the method of Bag and Egupov (modification of Raney's method) by leaching of a finely divided 50% nickel-aluminum alloy. This yielded a very active catalyst with a specific surface at 14 ± 1.5 m²/g. X-ray structural analysis showed that this catalyst contained some Al₂O₃ in addition to

metallic nickel. The catalyst was stored under water and loaded into the reaction in a moist state. As with the previous sample, before an experiment it was reduced with hydrogen at 500° and then outgassed. If dried in air it was much less active [8].

Laws of acetylene adsorption. Acetylene was adsorbed on both catalysts at 0° at an appreciable rate, which increased with an increase in temperature. The degree of filling of the surface of sample 1 by acetylene was low and represented 5-10% of a monolayer. On the other hand, the degree of filling on sample 2 reached 70% and more at room temperature. The adsorption of acetylene on Al_2O_3 was checked; it was low and did not exceed 2-3% of a monolayer. A considerable part of the acetylene, up to 40%, was not removed from the catalyst even with outgassing at 500°. After outgassing at 500°, re-adsorption was much less than the original adsorption. The kinetic law for adsorption on freshly prepared catalyst was readily reproducible and made it possible to determine the temperature dependence of adsorption. Figure 1 shows kinetic adsorption isotherms measured at 0 and 19.5° at similar starting pressures in the coordinates of common logarithms of adsorption, expressed in cc/g, and logarithms of time. It can be seen that with the exception of the initial adsorption, occurring in the first minute after the admission of gas, all the points in these coordinates lay on straight lines, whose slope increased with temperature.

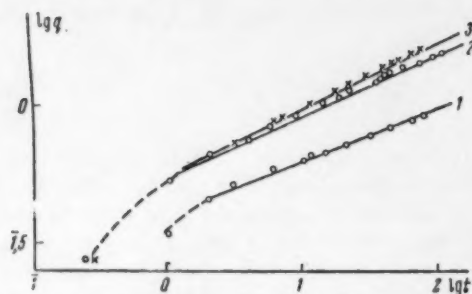


Fig. 1. Kinetic isotherms for the adsorption of acetylene on metallic nickel (sample 2):
1) Temperature 0°, pressure 4.48 mm;
2) temperature 19.5°, pressure 4.35 mm;
3) temperature 19.5°, pressure 4.45 mm.
(q-adsorption in cc/g; t-time).

Table 1 gives constants characterizing the kinetic isotherms, which satisfy the law

$$q = At^{1/n}, \quad (1)$$

derived from the statistical theory of processes on heterogeneous surfaces [9].

The change in activation energy, found by Roginskii's approximate equation from the displacement of the kinetic isotherms along the coordinate $RT \lg t$, coincided with that found from the Arrhenius equation (Fig. 2).

With an increase in the degree of filling of the surface from 0.256 to 2.56 cc/g, the activation energies increased from 11 to 18 kcal/mole. The rate of adsorption on sample 1 was considerably lower, but the law remained the same. This kinetic law indicates that the distribution of active centers with respect to adsorption energies is an exponential function.

Tracer methods make it possible to determine the proportions of the effects of heterogeneity and interaction on the change in adsorption activation energy.

Effect of heterogeneity. The effect of heterogeneity was investigated by the kinetic isotopic method. We measured the kinetic isotherm for the exchange of adsorbed C^{14} -labeled acetylene with acetylene of normal isotopic composition from the gas phase. Samples 1 and 2 were used for the investigation. In the first case the degree of filling by labeled acetylene was 7.4%. The exchange rate fell by a factor of 850 over 149 hr at 22° and at this stage only 22% of the adsorbed acetylene had exchanged, i.e., 0.75% of a monolayer. In another experiment on the same catalyst, the starting degree of filling was 3.7% of a monolayer. After 522 hr at 22° the rate of exchange fell by a factor of 3475. In this case the exchange rate was considerably lower. The exchange kinetics for these two experiments are shown in Fig. 3. With the exception of the first point, a plot of the kinetic

TABLE 1. Constants Characterizing the Kinetic Isotherms for Adsorption of Acetylene on Nickel (Sample 2)

Expt. No.	Temperature in °C	Pressure in mm Hg	1/n	$\alpha \cdot 10^4$ in (cal/mole) ⁻¹	lg A
1	19,5 ± 0,1	4,55	0,25	4,37	-0,26
2	19,5 ± 0,1	4,35	0,23	3,86	-0,25
3	0	4,48	0,21	3,85	-0,41
4	0	4,48	0,21	3,85	-0,41

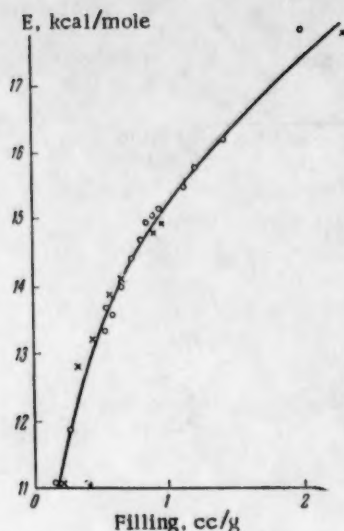


Fig. 2. Change in activation energy of acetylene adsorption with an increase in surface filling (sample 2): O—from Roginskii's equation; x—from Arrhenius' equation.

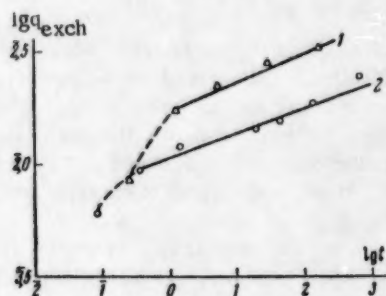


Fig. 3. Kinetic isotherms for the exchange of labeled acetylene adsorbed on Ni (sample 1): 1) Experiment 5, starting filling by labeled acetylene 7.4% of a monolayer; sample weight 0.54 g; $q_0 \text{ C}_2\text{H}_2^* = 0.3 \text{ cc}$; 2) experiment, 6, starting filling 3.7% of monolayer, sample weight 2.37 g; $q_0 \text{ C}_2\text{H}_2^* = 0.64 \text{ cc}$; temperature 22°; q —amount exchanged in cc; t —time in min.

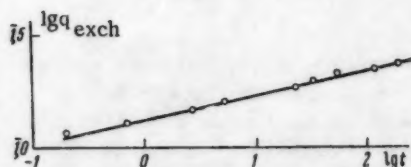


Fig. 4. Kinetic isotherm for the exchange of labeled acetylene adsorbed on Ni (sample 2); starting filling $q_0 \text{ C}_2\text{H}_2^* = 1.2 \text{ cc}$.

isotherm in the coordinates $\lg q$ and $\lg t$ was close to a straight line, indicating that Eq. (1) was obeyed in this case. The exchange kinetics on sample 2 were measured at room temperature. After 187 hr exchange, the rate constant, calculated from a first order equation, had fallen by a factor of 3400 and the amount of acetylene exchanged was 12% of that absorbed. Figure 4 shows the kinetic isotherm for the exchange of adsorbed acetylene in the same coordinates. In this case Eq.(1) was obeyed over a time range of more than three orders.

This study of the kinetic laws of exchange indicates the heterogeneity of the active surface with respect to acetylene adsorption. The kinetic laws for exchange and adsorption coincide and this implies that the forms of the distribution functions for active centers with respect to activation energies of exchange and adsorption also coincide.

Effect of "interaction." By the term "interaction" we mean the sum of the different effects that are able to produce a fall in the heats and activation energies of adsorption on a homogeneous surface. This includes the change proposed by De Boer and other changes in the work function of an electron in the metal due to the adsorption of a molecule in a charged state. The adsorption of acetylene on NiO is accompanied by a change in the electroconductivity, indicating charging due to the absorption of a positive charge. It is possible that on metallic nickel, acetylene is also an electron donor and is positively charged during adsorption. The role of interaction was investigated on sample 1. Labeled acetylene was adsorbed at room temperature on a catalyst sample which had been reduced with hydrogen and outgassed under standard conditions. The starting filling corresponded to 0.34% of a monolayer. The desorption kinetics were determined at room temperature. The rate of acetylene desorption was measured from the radioactivity of a barium carbonate precipitate obtained by combustion of the desorbed labeled acetylene, with a known amount of normal acetylene added as a carrier. The desorption rate fell by a factor of more than 30 in 2 hr. Table 2 gives the results of these experiments. After the additional adsorption, the degree of filling of the surface had increased by 40% in comparison with the original. Measurement of the rate of labeled acetylene desorption showed that after additional adsorption, it increased by a factor of almost 2, but remained a factor of 15 below the initial adsorption rate. The change in the degree of filling of the surface by labeled acetylene as a result of desorption was so small that it could be neglected. Two parallel experiments gave compatible results. The adsorption of the second portion of acetylene lasted for only 5 min and this eliminated the effect of redistribution of adsorbed labeled acetylene on the surface through the gas phase. This was confirmed by analysis of the residual unadsorbed acetylene for C^{14} content. No C^{14} was found. These data indicate that the change in activation energies and heats of adsorption with a change in the degree of filling of the surface by adsorbed acetylene is mainly connected with heterogeneity of the active surface and interaction has a weaker effect than heterogeneity.

TABLE 2. Rate of Desorption of Labeled Acetylene in Relation to the Total Filling of the Surface

Expt. No.	Adsorption	Desorption time in min	Desorption rate in cc/min·10 ⁵
7	C ¹⁴ - labeled acetylene, filling 0.34% of a monolayer	0-20	47,0
		20-50	8,0
	Additional adsorption of C ¹⁴ - free acetylene up to a filling of 0.43% of a monolayer	50-110	1,3
		0-20	2,4
		20-50	2,1
8	Starting filling by labeled acetylene of 0.4% of a monolayer	0-20	61,0
		20-50	9,4
		50-144	2,7
	Additional adsorption of normal acetylene up to a filling of 0.5% of a monolayer	0-21	3,9
		21-51	3,2
		51-117	3,2

EXPERIMENTAL RESULTS

The results of the investigation showed that the main reason for the fall in the heats and activation energies of adsorption is heterogeneity of the surface. In addition to heterogeneity, interaction also has an effect on these values. The low degree of filling of the surface of 0.4% makes it possible to assume that this effect is not connected with coulombic repulsion between two charged adsorbed molecules. At a filling of 0.4%, the adsorbed molecules lie at a distance of at least ten atoms from each other and coulombic interaction cannot be appreciable. Hence, it follows that interaction is connected with a change in other values and it is most probable that a layer of charged adsorbed particles, affecting the work function, is formed on the surface.

The concordance of the kinetic laws of acetylene adsorption and of the exchange of adsorbed labeled acetylene for normal acetylene from the gas phase indicates the absence of a simple connection between these processes. These laws indicate that in both cases there is a wide distribution of active centers with respect to the activation energies of the processes studied. If the exchange activation energy changed antipathetically with the change in the adsorption activation energy, i.e., the maximum adsorption activation energies corresponded to the minimum exchange activation energies, we would have had a contracting distribution with respect to exchange activation energies. In this case the kinetic exchange law would have differed from the kinetic adsorption law. The concordance of the laws indicates that the activation energies of adsorption and exchange change symbotically. This conclusion agrees with the absence of conformity between the exchange rate and the degree of filling of the surface in experiments in Fig. 2. The filling at the end of experiment 5 was higher than the initial filling in experiment 6, but the exchange rate in the latter case was higher than the exchange rate at the end of experiment 5. This may be explained by assuming that the highest exchange rate occurs on active sections with intermediate adsorption activation energies, corresponding to lower filling of the surface. This hypothesis agrees with the form of the relation between the activation energies of adsorption and desorption of acetylene on the same catalysts, observed in a study by the differential isotopic method [8]. A previous investigation unequivocally showed the presence of a minimum on the curve for the relation between the desorption activation energy and the adsorption activation energy. This type of relation between the activation energies of adsorption and exchange is apparently common, as in the investigation of many systems, it has been found that the kinetic law of exchange (1) coincides with kinetic law of adsorption of the same gas on the same catalysts. We studied the role of different adsorption centers in the hydrogenation of acetylene [8] on metallic nickel, and it was shown that the most active catalytic sites for hydrogenation of acetylene are active centers on which there is reversible adsorption, but adsorption with quite a strong bond.

In a study of metallic nickel (sample 1) by the differential isotopic method with respect to hydrogen adsorption with the use of hydrogen and deuterium [10], heterogeneity of the active surface was also observed. In investigating nickel catalysts deposited on silica gel and using the same differential isotopic method, Schmidt [11] was unable to detect heterogeneity. For this reason, Kwan [2] interpreted our results as a consequence of the use

of impure metallic nickel. Schmidt et al. [12] recently published a more careful investigation of the exchange of adsorbed deuterium for hydrogen on metallic nickel deposited on silica gel. The authors observed that adsorbed deuterium exchanged for hydrogen from the gas phase at different rates on different sections of the surface. A first order law was not obeyed, indicating that the active surface was heterogeneous. The ratio of HD , D_2 , and H_2 in the gas indicated the equilibrium of these forms under any condition. This may mean that the reaction $\text{H}_2 + \text{D}_2 = 2\text{HD}$ occurs on active centers which adsorb hydrogen weakly, as was established by Borekov and Vasilievich [13] for the exchange of H_2D_2 on a massive platinum catalyst. In the work of Schmidt et al., the kinetic exchange was measured over short periods of time. The ratio of the time of the last measurement to that of the first was 12. This fact makes it impossible to use these data for determining the kinetic exchange law and the nature of the distribution of active centers with respect to exchange activation energies, but, as the authors themselves admitted, it does indicate unequivocally the heterogeneity of the active surface of a metallic nickel catalyst. Eischens, Francis, and Pliskin [14] also observed the effect of heterogeneity and, simultaneously, interaction in an investigation of the chemisorption of CO on nickel deposited on nonporous silica gel. The investigation was carried out by observation of changes in the infrared spectra of adsorbed molecules with an increase in the degree of covering of the surface.

The sum of the data obtained by different authors for metallic nickel by investigating the adsorption of hydrogen, acetylene, and CO indicates the heterogeneity of the active surface of this catalyst and simultaneously shows the appreciable effect of interaction on the adsorption laws.

SUMMARY

1. The effect of heterogeneity and "interaction" on chemisorption of acetylene on metallic nickel was studied.
2. The change in the activation energies and heats of adsorption of acetylene with a change in the degree of filling of the surface by adsorbed acetylene is mainly connected with heterogeneity of the active surface. Interaction was found to have an appreciable, but weaker effect in comparison with heterogeneity.

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CHANGE IN THE COMPOSITION OF RADICALS IN A COMPLEX CHAIN REACTION

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At the basis of Semenov's theory of degenerate branching [1] lies the idea of the determining effect of the products of a chain reaction on its rate. The mechanism of degenerate branching consists of simple chain initiation due to the molecular reaction products formed. However, degenerate branching is not the only means whereby the molecular products of a reaction can affect its rate. Molecular products accumulating during the reaction inevitably react with free radicals and change their composition and over-all activity and thus affect the rate of the chain reaction. This situation was given a theoretical basis in [2, 3] and is a further development of the theory of degenerate-branched chain reactions. An actual change in the over-all activity of radicals during a chain reaction was recently established experimentally on the example of liquid-phase oxidation of cyclohexane [4].

The problem of the change in the rate of an unbranched chain reaction due to the change in the composition of the radicals was examined in a simplified form in [2] and it was assumed that chain termination occurred with one sort of free radical. Therefore, the formulas derived are accurate only for a small degree of replacement of the original free radicals by free radicals from the reaction products. The change in the kinetics of a degenerate-branched chain reaction due to a change in the composition of the radicals was examined in [3]. The problem of the change in the over-all activity of the radicals was solved for the case of two active centers in this work. However, most chain oxidation reactions are characterized by the formation of not one but several molecular products and each of these can introduce into the reaction its own sort of free radical. Therefore, it is necessary to examine the problem of the change in the composition of radicals in a complex chain reaction for the general case when several molecular products are formed from the starting material and each of these introduces its own sort of free radicals into the reaction. The present work is devoted to this problem.

Let us examine the change in composition of the radicals in the oxidation of the hydrocarbon RH. Let us suppose that as a result of oxidation of the hydrocarbon there are m products formed that are successively converted from one to another: $P_1, \dots, P_i, \dots, P_m$, and the relative concentrations of these we will denote by $\pi_1, \dots, \pi_i, \dots, \pi_m$, where $\pi_i = [P_i]/[RH]$. During the chain reaction, each of these products supplies its own sort of free radicals, which participate in the chain propagation reaction. Let us denote the concentration of the free radicals formed from the hydrocarbon and responsible for the oxidation by n_0 (these will be the radicals $ROO\cdot$) those from P_i by n_i , and the fractions of these free radicals by n'_0, n'_1, n'_m , where $n'_1 = n_1/n$.

$$n = \sum_{i=0}^m n_i.$$

Each sort of radical i has its characteristic rate constant for reaction with a given product P_j , k_{ij} . It is advantageous to introduce relative values of the constants by dividing the values k_{ij} by k_{00} , i.e., the rate constant for reaction of the radicals $ROO\cdot$ formed from the hydrocarbon with the hydrocarbon itself: $\alpha_{ij} = k_{ij}/k_{00}$. The rate of oxidation of the hydrocarbon in the developed reactions is given by the expression

$$-\frac{d[RH]}{dt} = k_{00}[RH]n_0 + \dots + k_{i0}[RH]n_i + k_{m0}[RH]n_m =$$

$$= k_{00}[RH]n \sum_{i=0}^m \alpha_{i0} n'_i = k_{00}[RH]n\varphi,$$

where φ is a function characterizing the change in the relative activity of the mixture of free radicals due to the change in their composition. The solution of the problem of the change in activity of the radicals during the reaction is reduced to finding the form of the function φ and since $\varphi = \sum \alpha_{i0} n_i$, it is necessary to find expressions for all n'_i . With sufficiently long chains, a stationary state of the reaction, and identical rates of chain termination for different free radicals, the concentration of a given form of radical i is determined by the rate of their formation and consumption in chain propagation reactions. Free radicals i are formed as a result of reactions of all the other radicals with product P_i and are consumed as a result of reactions with all the other products apart from P_i . For the rate of accumulation of radicals i , which equals zero in the stationary state, we may write the equation

$$\frac{dn_i}{dt} = \sum_{\substack{j=0 \\ j \neq i}}^m n_j k_{ji} [P_i] - \sum_{\substack{j=0 \\ j \neq i}}^m n_i k_{ij} [P_j] = 0,$$

which is written in the following form in dimensionless variables:

$$\pi_i \sum_{j=0}^m n'_j \alpha_{ji} - n'_i \sum_{j=0}^m \alpha_{ij} \pi_j = 0 \quad (j \neq i).$$

As there are $m+1$ active centers, we obtain $m+1$ such equations. Only m of these equations will be nonlinearly dependent. By adding to these m equations the equation $\sum n'_i = 1$, we obtain a heterogeneous system of $m+1$ linear equations with $m+1$ unknowns

$$n'_0 + n'_1 + \dots + n'_i + \dots + n'_m = 1$$

$$\alpha_{01} \pi_1 n'_0 - n'_1 \sum_{\substack{j=0 \\ j \neq 1}}^m \alpha_{1j} \pi_j + \dots + \alpha_{i1} \pi_1 n'_i + \dots + \alpha_{m1} \pi_1 n'_m = 0$$

.....

$$\alpha_{0j} \pi_j n'_0 + \alpha_{1j} \pi_j n'_1 + \dots - n'_i \sum_{\substack{j=0 \\ j \neq i}}^m \alpha_{ij} \pi_j + \dots + \alpha_{mj} \pi_j n'_m = 0$$

.....

$$\alpha_{0m} \pi_m n'_0 + \alpha_{1m} \pi_m n'_1 + \dots + \alpha_{im} \pi_m n'_i + \dots - n'_m \sum_{\substack{j=0 \\ j \neq m}}^m \alpha_{mj} \pi_j = 0.$$

The determinant of this system of equations $D \neq 0$ and consequently the system is determinable and has only one solution. The unknowns n'_i are expressed by Kramer's formulas:

$$n'_i = \frac{D_i}{D},$$

where

$$\begin{aligned}
 D &= \begin{vmatrix} 1 & 1 & \dots & 1 & \dots & 1 \\ \alpha_{01}\pi_1 - \sum_{\substack{j=0 \\ j \neq 1}}^m \alpha_{1j}\pi_j & \dots & \alpha_{l1}\pi_1 & \dots & \alpha_{m1}\pi_1 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{0j}\pi_j & \alpha_{1j}\pi_j & \dots & - \sum_{\substack{j=0 \\ j \neq i}}^m \alpha_{ij}\pi_j & \dots & \alpha_{mj}\pi_j \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{0m}\pi_m & \alpha_{1m}\pi_m & \dots & \alpha_{lm}\pi_m & \dots & - \sum_{j=0}^m \alpha_{ij}\pi_j \end{vmatrix} \\
 D_l &= \begin{vmatrix} 1 & 1 & \dots & 1 & \dots & 1 \\ \alpha_{01}\pi_1 - \sum_{\substack{j=0 \\ j \neq 1}}^m \alpha_{1j}\pi_j & \dots & 0 & \dots & \alpha_{m1}\pi_1 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{0j}\pi_j & \alpha_{1j}\pi_j & \dots & 0 & \dots & \alpha_{mj}\pi_j \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{0m}\pi_m & \alpha_{lm}\pi_m & \dots & 0 & \dots & - \sum_{j=0}^{m-1} \alpha_{ij}\pi_j \end{vmatrix} = \\
 &= (-1)^{(1+l)} \begin{vmatrix} \alpha_{01}\pi_1 & \dots & \alpha_{l-1,1}\pi_1 & \alpha_{l+1,1}\pi_1 & \dots & \alpha_{m1}\pi_1 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{0j}\pi_j & \dots & \alpha_{l-1,j}\pi_j & \alpha_{l+1,j}\pi_j & \dots & \alpha_{mj}\pi_j \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{0m}\pi_m & \alpha_{l-1,m}\pi_m & \alpha_{l+1,m}\pi_m & \dots & - \sum_{j=0}^{m-1} \alpha_{ij}\pi_j \end{vmatrix} = A_{1l}.
 \end{aligned}$$

Knowing the values of n'_i as functions of α_{ij} and π_j , it is possible to find φ .

$$\varphi = \sum_{i=0}^m \alpha_{i0} n'_i = \frac{1}{D} \sum_{i=0}^m \alpha_{i0} D_i.$$

If the activities of all the radicals are identical, then, as would be expected, $\varphi = 1$, since

$$D = \sum_{i=0}^m D_i.$$

Quite a simple expression for φ is obtained when the relative activity of free radicals \underline{i} with respect to different products \underline{j} remains constant, i.e., there is a constant relation

$$\frac{k_{ij}}{k_{0j}} = \frac{k_{i0}}{k_{00}}$$

or

$$\alpha_{i0} \cdot \alpha_{0j} = \alpha_{ij}. \quad (1)$$

Such a relation occurs in those cases when all the chain propagation reactions, i.e., exchange reactions between all radicals i and products j , are either exothermal or endothermal. Let us examine this problem in more detail. Each reaction rate constant may be expressed in the form: $k_{ij} = k_{ij}^0 \exp(-E_{ij}/RT)$. It may be shown from experimental data that in an overwhelming majority of cases the preexponential terms for replacement reactions by peroxide radicals depend linearly on E and relation (1) is reduced to the following relation between the activation energies:

$$E_{i0} - E_{00} = E_{ij} - E_{0j}, \quad (2)$$

where E_{ij} is the activation energy for the reaction of free radical i with product j . By using Polanyi's equation for the relation between E and the heat effect of the reaction [5], it is possible to establish when Eq. (2) is actually true. By using Q_i to denote the energy of the bond formed as a result of abstraction of an H-atom by radical i and Q_j for the energy of the bond ruptured in product j . If all the reactions of radicals i with products j are exothermal, then all the values $E_{ij} = 11.5 - 0.25(Q_i - Q_j)$, and instead of Eq. (2) we obtain the equation:

$$(Q_i - Q_0) - (Q_0 - Q'_0) = (Q_i - Q'_j) - (Q_0 - Q'_j),$$

which is the same as

$$Q_i - Q_0 = Q_i - Q_0.$$

An analogous result is obtained in the case when all the chain propagation reactions are endothermal. In this case, for each elementary reaction, $E = 11.5 + 0.75q$ and Eq. (2) is also obeyed. In cases when there are both exothermal and endothermal chain propagation reactions in the reaction system, Eq. (2) and consequently Eq. (1) are not fulfilled. These and other cases are possible in actual oxidation processes.

If only two products are formed from a hydrocarbon (one an intermediate and the other the final product) and Eq. (1) is fulfilled, then for φ we obtain the following simple expression:

$$\varphi = \frac{\begin{vmatrix} (-\alpha_{10} - \alpha_{12}\pi_2) \alpha_{21}\pi_1 \\ \alpha_{12}\pi_2 (-\alpha_{20} - \alpha_{21}\pi_1) \end{vmatrix} - \alpha_{10} \begin{vmatrix} \alpha_{01}\pi_1 \alpha_{21}\pi_1 \\ \alpha_{02}\pi_2 (-\alpha_{20} - \alpha_{21}\pi_1) \end{vmatrix} + \alpha_{20} \begin{vmatrix} \alpha_{01}\pi_1 (-\alpha_{10} - \alpha_{12}\pi_2) \\ \alpha_{02}\pi_2 \alpha_{12}\pi_2 \end{vmatrix}}{\begin{vmatrix} (-\alpha_{10} - \alpha_{12}\pi_2) \alpha_{21}\pi_1 \\ \alpha_{12}\pi_2 (-\alpha_{20} - \alpha_{21}\pi_1) \end{vmatrix} - \begin{vmatrix} \alpha_{01}\pi_1 \alpha_{21}\pi_1 \\ \alpha_{02}\pi_2 (-\alpha_{20} - \alpha_{21}\pi_1) \end{vmatrix} + \begin{vmatrix} \alpha_{01}\pi_1 (-\alpha_{10} - \alpha_{12}\pi_2) \\ \alpha_{02}\pi_2 \alpha_{12}\pi_2 \end{vmatrix}} \\ \varphi = \frac{1 + \alpha_{01}\pi_1 + \alpha_{02}\pi_2}{1 + \frac{\alpha_{01}}{\alpha_{10}}\pi_1 + \frac{\alpha_{02}}{\alpha_{20}}\pi_2}. \quad (3)$$

For the case of m products with fulfillment of relation (1), we obtain the formula:

$$\varphi = \left(1 + \sum_{j=1}^m \alpha_{0j}\pi_j \right) / \left(1 + \sum_{j=1}^m \frac{\alpha_{0j}}{\alpha_{j0}}\pi_j \right).$$

Each product π_j , reacting with free radicals, is, strictly speaking, an intermediate since it is formed and consumed by a chain mechanism. Therefore, its concentration cannot exceed a limiting concentration, determined from the equation

$$\frac{d\pi_j}{dt} = k_{00} [RH] n\varphi - k_{00} [RH] n\pi_j \sum_{i=0}^m \alpha_{ij}n'_i = 0,$$

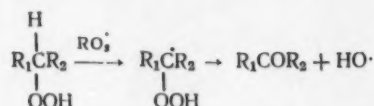
whence $(\pi_j)_{\max} = \frac{\varphi}{\sum_i \alpha_{ij} n_i'} = \frac{\varphi}{\alpha_{0j} \sum_i \alpha_{i0} n_i'} = \frac{1}{\alpha_{0j}}$, since $\varphi = \sum_i n_i' \alpha_{i0}$. By substituting $1/\alpha_{0j}$ in the expression for φ instead of π_j , we obtain

$$\varphi' = \left(1 + \sum_j \alpha_{0j} \frac{1}{\alpha_{0j}} \right) / \left(1 + \sum_j \frac{\alpha_{0j}}{\alpha_{j0}} \frac{1}{\alpha_{0j}} \right) = (1 + m) / \left(1 + \sum_j \frac{1}{\alpha_{j0}} \right), \quad (4)$$

where φ' is the limiting value to which φ tends during the reaction.

Two extreme cases are possible. If more active radicals for which $\alpha_{j0} > 1$ are formed from the oxidation products, then at sufficiently high values of α_{j0} , the sum of their reciprocals will be less than unity and $\varphi' \leq 1 + m$. Consequently, the appearance of more active radicals in the system cannot increase the rate of the chain propagation reaction by a factor of more than $m + 1$ regardless of the activity of the new free radicals. A completely different picture is obtained when less active radicals accumulate. In this case $\alpha_{j0} < 1$ and $\sum [1/\alpha_{j0}] > 1$. If the radicals are very inactive, then $\sum [1/\alpha_{j0}] \gg 1$ and φ' may be any small value. Consequently, the accumulation of products giving radicals of low activity in the chain reaction may retard this reaction to any extent. This interesting conclusion again emphasized the importance of a change in the composition of the radicals in self-retarding complex chain reactions.

At the present time there are no reliable data on precisely the nature of free radicals formed in a chain oxidation from the molecular products. There are more or less substantiated hypotheses. Nonetheless, it seemed interesting to examine this problem even if only to make a qualitative assessment of the difference in activity between different radicals whose formation may be postulated. The oxidation of hydrocarbons proceeds through the formation of the peroxide radical $\text{ROO}\cdot$. The first molecular intermediate product of the low-temperature oxidation of hydrocarbons is hydroperoxide. The chain decomposition of a secondary hydroperoxide apparently proceeds in the form of a sequence of elementary acts

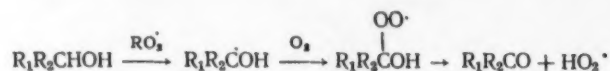


and leads to the replacement of $\text{ROO}\cdot$ radicals by more active hydroxyl radicals. The ratio of the activities of these radicals equals $\exp(\Delta E/RT)$

$$\Delta E = 0,25(Q_{\text{HO-H}} - Q_{\text{RO}_2\text{-H}}) = 0,25(118-90) = 7 \text{ kcal/M}.$$

At $T = 400^\circ$, the exponential equals 6300, i.e., the hydroxyl radical is much more active than the peroxide radical.

Oxidation of secondary and primary alcohols apparently proceeds in the following way:



The radical $\text{ROO}\cdot$ is replaced by the radical $\text{R}_1\text{R}_2\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{OO}\cdot \end{array}$ or the radical $\text{HO}_2\cdot$. In the oxidation of the ketone

$\text{R}_1\text{CH}_2\text{COR}_2$, instead of the radical $\text{ROO}\cdot$, the radical R_1CHCOR_2 is formed. In the oxidation of the aldehyde RCHO , the radical $\text{RC} \begin{array}{l} \text{O} \\ \diagup \\ \text{OO}\cdot \end{array}$ is formed.

At the present time it is assumed that the energy for rupturing the bond ROO-H is independent of the nature of the radical R. This assumption is only justifiable in the first approximation. It may be expected that there

will be a relation between the energy of the ROO-H bond and the nature of R and the activities of different peroxide radicals may differ from each other several-fold.

As has already been stated, the reaction rate may fall particularly strongly due to a change in the composition of the radicals. However, for this to occur, products giving radicals of very low activity must accumulate in the reaction. In particular, such products may be phenolic compounds, many of which are inhibitors of chain oxidation reactions. Such phenolic products are formed in liquid-phase oxidation of alkylaromatic hydrocarbons; they introduce into the reaction practically inactive phenoxy radicals, which strongly reduce the rate of the chain propagation reaction. Thus, in the oxidation of some hydrocarbons, for example, paraffins, one would expect a comparatively small (within the limits of one order) change in the reaction rate due to a change in the composition of the radicals. In the oxidation of other hydrocarbons, for example, alkylaromatic hydrocarbons, one would expect a considerable decrease in the reaction rate due to the accumulation of radicals of low activity.

The various kinetic characteristics of a degenerate branched reaction connected with a change in the activity of the radicals were examined in [3] for the case of two active centers. These characteristics will also be found in the case of several active centers if the activity of the new free radicals changes monotonically during the whole of the reaction. Fundamentally new kinetic characteristics should be observed in cases when some of the products form more active radicals and others form less active radicals.

Let us examine a chain reaction with one intermediate and one final product with linear chain termination and degenerate branching at the intermediate product: $RH \rightarrow P \rightarrow K$. For the rates of accumulation of the intermediate and final products, we obtain the following differential equations:

$$\frac{d[P]}{dt} = (k_{00}[RH] - k_{01}[P]) n\varphi \quad \frac{d[K]}{dt} = k_{01}[P] n\varphi$$

$$n = \frac{w_0 + k[P]}{k_{\text{ter}}},$$

where w_0 is the constant rate of chain initiation, k is the rate constant of degenerate branching, and k_{ter} is the rate constant of linear termination. Converting to the dimensionless variables

$$\pi = \frac{[P]}{[RH]}, \quad \xi = \frac{[K]}{[RH]}, \quad \tau = \frac{k_{00}k[RH]}{k_{\text{ter}}} t, \quad w_0 = \frac{w_0}{k[RH]},$$

we obtain the equation

$$\frac{d\pi}{d\tau} = (1 - \alpha_{01}\pi)(w_0 + \pi)\varphi \quad (5)$$

$$\frac{d\xi}{d\tau} = \alpha_{01}\pi(w_0 + \pi)\varphi. \quad (6)$$

According to formula (3)

$$\varphi = \frac{1 + \alpha_{01}\pi + \alpha_{02}\xi}{1 + \frac{\alpha_{01}}{\alpha_{10}}\pi + \frac{\alpha_{02}}{\alpha_{21}}\xi}.$$

Let us examine the case when the intermediate product forms more active radicals and the final product, which, strictly speaking, is an intermediate product forms less active radicals than the original radicals ROO. Figure 1 shows the course of kinetic curves of π and ξ , obtained by numerical integration of equations (5) and (6) with the following values for the constants: $w_0 = 0.001$, $\alpha_{01} = 20$, $\alpha_{02} = 5$, $\frac{\alpha_{01}}{\alpha_{10}} = 2$, $\frac{\alpha_{02}}{\alpha_{21}} = 10$.

The change in the over-all activity of the radicals is also shown in Fig. 1. The over-all activity of the radicals passes through a maximum during the reaction. Precisely this result was obtained experimentally in a study of the oxidation of cyclohexane [4]. Figure 2 shows kinetic curves of the accumulation of cyclohexanone (the main intermediate product) and dicarboxylic acids (the main final product) in the oxidation of cyclohexane at 140° and 30 atm. Figure 2 also shows the relative change in the over-all activity of the radicals during the reaction, established by inhibition of the reaction during its course. It is clearly seen that the over-all activity of the radicals passes through a maximum during the oxidation of cyclohexane. This experimental fact is explained by the scheme above.

The opposite case when the intermediate product forms less active radicals and the final product gives more active radicals is also possible theoretically. The over-all activity of the radicals will then pass through a minimum during the reaction (Fig. 3).

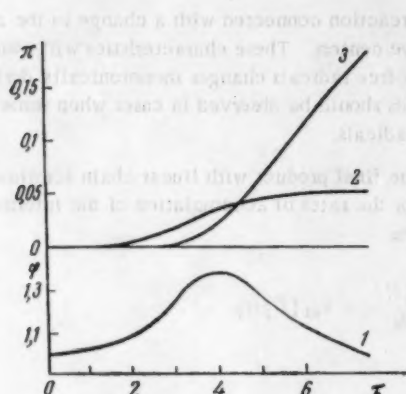


Fig. 1. Change in the over-all activity of the radicals $\varphi = \frac{1 + 20\pi + 5\xi}{1 + 2\pi + 10\xi}$

(1) and kinetic curves of π (2) and ξ (3), calculated from equations (5) and (6) for $\omega_0 = 0.001$.

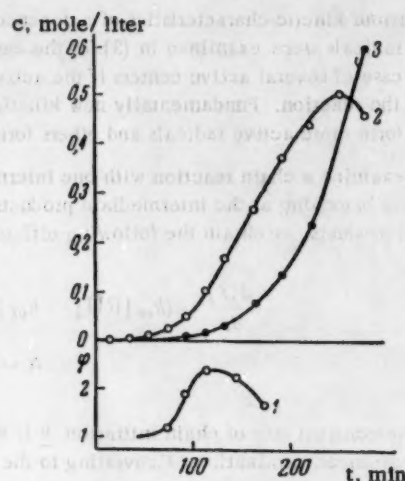


Fig. 2. Change in over-all activity of the radicals (1) and kinetic curves of the accumulation of cyclohexanone (2) and dicarboxylic acids (3) in the oxidation of cyclohexane at 140° and 30 atm.

The changing composition of the radicals affects not only the over-all activity of the radicals, but also their total concentration by changing the rate of second-order chain termination. Each sort of free peroxide radical is characterized by its own rate constant for reaction with another k'_{ij} the range of variation in these is $10^8 - 10^4$ liter/mole-sec. The relative change in the total concentration of free radicals due to a change in their composition equals

$$\varphi_g = \left(\frac{k'_{00} n^2}{\sum_{ij} k'_{ij} n_i n_j} \right)^{\frac{1}{2}} = \left(\sum_{ij} \alpha'_{ij} n_i n_j \right)^{-\frac{1}{2}},$$

where $\alpha'_{ij} = \frac{k'_{ij}}{k'_{00}}$. For simplifying the calculation we assume that the activities of all radicals are the same ($\alpha_{ij} = \alpha_{0j}$), and $\alpha'_{ij} = (\alpha'_{ii} \alpha'_{jj})^{\frac{1}{2}}$. Then $\varphi_g = \frac{\sum \alpha_{0i} \pi_i}{\sum \sqrt{\alpha'_{ii} \alpha_{0i} \pi_i}}$, while in a developed reaction when $\pi_i = \frac{1}{\alpha_{0i}}$, $\varphi_g = \frac{1+m}{1+\sum \sqrt{\alpha'_{ii}}}$. If all the i free radicals react with each other very slowly, then $\varphi_g \approx 1+m$ (the upper limit of φ_g). If at least one of them reacts very rapidly, then this may retard the reaction very strongly:

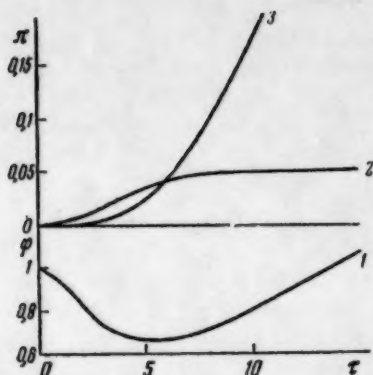


Fig. 3. Change in the over-all activity of the radicals

$$\varphi = \frac{1 + 20\pi + 5\xi}{1 + 50\pi + 0.5\xi}$$

(1) during the reaction and kinetic curves of π (2) and ξ (3), calculated from equations (5) and (6) for $\omega_0 = 0.001$

$$\left(\varphi g \approx \frac{1+m}{1+\sqrt{\alpha_{II}}} \right).$$

Thus, the mechanism of the effect of radical composition on the rate of a complex chain reaction is such that the acceleration of the reaction is limited, while it can be retarded to any extent. In our opinion, this is the fundamental reason for the widespread phenomenon of self-retarding oxidation reactions.

SUMMARY

1. In complex chain reactions involving the formation of molecular intermediate products, the composition of the radicals inevitably changes during the reaction due to the change in the composition of the products. A general solution was obtained in the present work for the problem of the change in the rate of a complex chain reaction due to a change in the composition of the radicals for the case of several active centers.

2. The appearance of more active radicals in the reaction mixture may increase the reaction rate by a limited factor, while the appearance of radicals of low activity may retard the chain reaction very strongly.

3. Radicals which react very slowly with each other accelerate the reaction by a limited factor, while radicals which react with each other rapidly may retard the reaction very strongly.

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CHAIN-THERMAL PROPAGATION OF FLAME

COMMUNICATION 2. EFFECT OF PRESSURE AND TEMPERATURE

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In the first article [1] we obtained a relation for determining the flame propagation velocity in a system with a simplified chain reaction scheme from an analysis of the heat conductivity equation and the equation for active center diffusion. After further simplification we obtained a more approximate and a simpler formula:

$$u_0 = \frac{1}{\rho_0} \sqrt{\frac{n_r Q_m (\rho D_p)_m}{2cT_r}} = \frac{1}{2\rho_0} \sqrt{n_r K_m (\rho D_p)_m}, \quad (1)$$

where ρ_0 is the mixture density at the initial temperature T'_0 in $^{\circ}\text{K}$, n_r is the concentration of the active center at the combustion temperature $T'_r = T_r + T'_0$, c is heat capacity, $(\rho D_p)_m$ is the product of the mixture density and the diffusion coefficient for the active center at temperature T_m , which corresponds to the maximum value of the temperature gradient; $n_m Q_m = n_m h n_A m K_m$ is the rate of heat evolution; h is the heat effect of the reaction; n_A is the concentration of the starting material; $K_m = Z_A \frac{1}{\mu_p} \rho_m^2 \exp(-E/RT'_m)$ is the rate constant of the reaction; and μp is the molecular weight of the active center.

The problems in the present article do not require a more accurate relation for u_0 . Considering that [1]

$$T'_m = \frac{T'_r + T'_0}{2} \text{ and } \rho_m = \rho_0 \frac{\mu_m}{\mu_0} \frac{T'_0}{T'_m},$$

where μ is the apparent molecular weight of the mixture, from [1] we obtain

$$u_0 = \sqrt{n_r (\rho D_p)_m Z_A \frac{\mu_m^2}{\mu_p \mu_0^2} \left(\frac{T'_0}{T'_r + T'_0} \right)^2 \exp[-2E/R(T'_r + T'_0)]}. \quad (2)$$

Denoting values in the initial state by the subscript "H" and values in the new state by the subscript "L" and assuming that $D_p \sim (T')^a$, we obtain from (2) a conversion ratio for the flame propagation velocity under the new conditions:

$$\begin{aligned} \frac{u_{0L}}{u_{0H}} &= \left[\frac{T'_{0L}(T'_{rH} + T'_{0H})}{T'_{0H}(T'_{rL} + T'_{0L})} \right]^{\frac{3-a}{2}} \left(\frac{\mu_{mL} \mu_{0H}}{\mu_{mH} \mu_{0L}} \right)^{\frac{3}{2}} \sqrt{\frac{n_{rL}}{n_{rH}}} \times \\ &\times \exp \left[\frac{E}{R} \left(\frac{1}{T'_{rH} + T'_{0H}} - \frac{1}{T'_{rL} + T'_{0L}} \right) \right]. \end{aligned} \quad (3)$$

The concentration of the active center n_r may be expressed through the equilibrium constant $K_P = P_r^2/P_A$, where P_Σ is the total pressure of the mixture while the corresponding partial pressures are determined by the relations

$$P_P = P_\Sigma n_r \frac{\mu_r}{\mu_P} \text{ and } P_A = P_\Sigma n_A \frac{\mu_r}{\mu_A}.$$

Taking this into consideration, we find for the root of the concentration ratio:

$$\sqrt{\frac{n_{rL}}{n_{rH}}} = \sqrt{\frac{K_{PL} \mu_{rL} n_{AL}}{K_{PH} \mu_{rH} n_{AH}}} \sqrt{\frac{P_{\Sigma H}}{P_{\Sigma L}}}. \quad (4)$$

The equilibrium constant is determined by the relation [2]:

$$R \ln K_P = - \frac{\Delta Z^0}{T'} = \Delta \Phi^* - \frac{\Delta H_0^0}{T'}, \quad (5)$$

where Z^0 is the isobar-isotherm potential; Φ^* is the temperature-dependent part of the Planck thermodynamic potential; ΔH_0^0 is the hypothetical heat effect of the reaction at 0°K. From (5) we obtain:

$$\frac{K_{PL}}{K_{PH}} = \exp \left[\frac{\Delta \Phi_L^* - \Delta \Phi_H^*}{R} \right] \exp \left[- \frac{\Delta H_0^0}{R} \left(\frac{1}{T_{rL}'} - \frac{1}{T_{rH}'} \right) \right]. \quad (6)$$

In approximate calculations and with a small range of temperature changes, the difference $(\Delta \Phi_L^* - \Delta \Phi_H^*)$ may be neglected and we may consider that

$$\frac{K_{PL}}{K_{PH}} \approx \exp \left[- \frac{\Delta H_0^0}{R} \left(\frac{1}{T_{rL}'} - \frac{1}{T_{rH}'} \right) \right]. \quad (7)$$

The pressure dependence of the flame propagation velocity.

As Fiock [3] noted the experimental data on the pressure dependence of the flame propagation velocity is very contradictory. The state of this problem is examined in detail in the review by Thomas [4]. Recent investigations [5-7] have been directed towards the elimination of systematic deviations of measurements, connected with an increase in the width of the reaction zone at low pressures. In Thomas' review [4] and in the article by Egerton and Lefebvre [5] the dependence of u_0 on pressure is discussed on the basis of thermal and diffusion theories. Thermal theories for a second-order reaction predict that the propagation velocity will be pressure-independent, as may be seen in the table in review [5]. It follows from the diffusion theory of Tanford and Pease that $u_0 \sim (P_\Sigma)^{-0.25}$, while from the diffusion theory of Gaydon and Wolfhard, u_0 is independent of pressure. A number of remarks on the assumptions adopted in diffusion theories are made in the review [4]. Noting that on the whole the diffusion theory of Tanford and Pease gives the best agreement with experiment, Egerton and Lefebvre [5] conclude that "on comparing the results obtained with the pressure dependence derived from the thermal and diffusion theories, one is convinced that it is impossible to give an explanation satisfying all requirements on the basis of one particular theory. If one assumes that flame propagation simultaneously consists of heat and diffusion processes, with the hydrogen atoms assuming special importance in rich mixtures, then evidently, the results may be understood."

In the present work we attempt to apply the formula derived in article [1] not to the calculation of absolute values of u_0 in hydrocarbon fuel mixtures but to the determination of the change in propagation velocities with a change in pressure from relation (3). Without considering the detailed mechanism of the chemical conversion, we will assume that the form of the rate constant of heat evolution K remains unchanged with pressure changes.

Using data in [8] for starting mixtures of ethylene and air, we determined the relations of the dimensionless weight concentrations of H, O, and OH and the combustion temperatures with pressure changes from $P_{\Sigma} = 10$ atm to $P_{\Sigma} = 0.01$ atm and changes in the excess fuel coefficient β from 0.5 to 3.0. These data are given in Figs. 1 and 2 in logarithmic coordinates. Using these data, the theoretical dependence of u_0 on pressure may be calculated by equation (3). The calculation of the compositions of such a mixture requires the solution of a system of eleven nonlinear equations and is quite laborious. Therefore, in the absence of accurate data on the compositions, the relations (4) and (7) may be used, with the approximate assumption that $\mu_L \approx \mu_H$ and $n_{AL} \approx n_{AH}$ in them. With a change in pressure from $P_{\Sigma} = 1.0$ atm to $P_{\Sigma} = 0.01$ atm, the molecular weight of the combustion products μ_T decreases by not more than 1.5% in strongly dissociated mixtures when $\beta = 1-1.2$. The change in n_A with pressure depends on the composition of the mixture. In converting the H atom concentration by relation (4), one may assume with sufficient accuracy that $n_{H_2} = \text{const.}$ only for rich mixtures ($\beta > 1$), while in converting the O concentration n_{O_2} remains practically constant for only lean mixtures. The error in μ_0 , due to neglecting the change in n_{H_2} from $P_{\Sigma} = 1.0$ atm to $P_{\Sigma} = 0.1$ atm, was $\delta_u = 10\%$ when $\beta = 1$ ($\delta_u = 2.5\%$ when $\beta = 1.2$ and $\delta_u = 0.2\%$ when $\beta = 1.5$). The error in μ_0 due to neglecting the change in n_{O_2} over the same range, was $\delta_u = 10\%$ when $\beta = 1$ ($\delta_u = 1\%$ when $\beta = 0.8$).

If with a decrease in pressure the combustion temperature hardly changes, as usually occurs at combustion temperatures of $T_f < 1800^\circ\text{K} - 2000^\circ\text{K}$, then for this case a simple pressure dependence may be obtained for u_0 from relation (3) and taking (4) into consideration

$$\frac{u_{0L}}{u_{0H}} = \sqrt[4]{\frac{n_{AL}}{n_{AH}}} \sqrt[4]{\frac{P_{\Sigma H}}{P_{\Sigma L}}} \approx \sqrt[4]{\frac{P_{\Sigma H}}{P_{\Sigma L}}}. \quad (8)$$

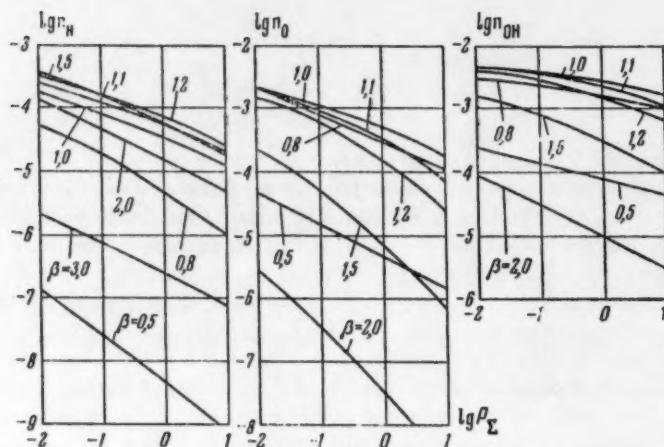


Fig. 1. Relations of H, O, and OH concentrations (in g/g of mixture) at combustion temperatures to pressure (atm) for ethylene-air mixtures at an initial temperature of $T_0 = 300^\circ\text{K}$; $\beta = L/L$ stoich.; L is the weight ratio of fuel to air.

Diederichsen and Wolfhard [6] measured the dependence of u_0 for methane-air and methane-oxygen mixtures over a wide range of pressure changes, and established that for a stoichiometric methane-oxygen mixture u_0 was independent of pressure over the range $P_{\Sigma} = 2$ atm to $P_{\Sigma} = 0.05$ atm. The pressure dependences of the combustion temperature and of the H, O, and OH concentrations are given in [6] for the mixtures investigated. If we assume that H atoms have the leading role in flame propagation [4, 5], neglect the change in molecular weight μ_m , and take the value $a = 1.75$ for the exponent of the temperature dependence of the diffusion coefficient, from

the data in [6] and using relation (3) we may determine the effective activation energy E . It was found that for a stoichiometric methane-oxygen mixture $E = 13.7$ kcal/mole over the pressure range from $P_{\Sigma} = 1$ atm ($T_r' = 3049^\circ\text{K}$) to $P_{\Sigma} = 0.01$ atm ($T_r' = 2543^\circ\text{K}$). According to experimental data given in [6], for a stoichiometric methane-air mixture from $P_{\Sigma} = 1$ atm to $P_{\Sigma} = 0.1$ atm, the exponent \underline{k} in the empirical relation $u_0 \sim P_{\Sigma}^{\underline{k}}$ equals -0.20 . The theoretical mean value of exponent \underline{k} , calculated for these conditions by relation (3) when $E = 13.7$ and using the pressure dependences of the H concentration and temperature T_r' from [6], was found to be -0.21 .

Gilbert [7] determined the value of exponent \underline{k} as -0.18 for an ethylene-air mixture when $\beta = 1.2$ and from $P_{\Sigma} = 1$ atm to $P_{\Sigma} = 0.1$ atm. From this value of \underline{k} and the data given in Figs. 1 and 2, using relation (3) we found that $E = 5$ kcal/mole. After this the change in exponent \underline{k} from $\beta = 0.5$ to $\beta = 3.0$ was calculated from (3). This result is given in Fig. 3 (denoted by n_H). The values of \underline{k} are practically independent of the value of E for lean

($\beta < 0.8$) and rich ($\beta > 1.5$) mixtures. Let us examine the relation of exponent \underline{k} to a change in the value of E when $\beta = 1.2$: when $E = 0$, $\underline{k} = -0.19$, when $E = 10$, $\underline{k} = -0.17$, and when $E = 20$, $\underline{k} = -0.15$.

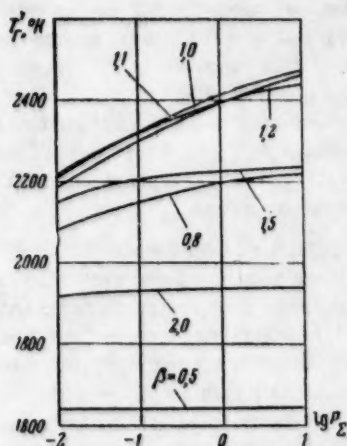


Fig. 2. Pressure dependence of the combustion temperature T_r' for ethylene-air mixtures at $T_0 = 300^\circ\text{K}$.

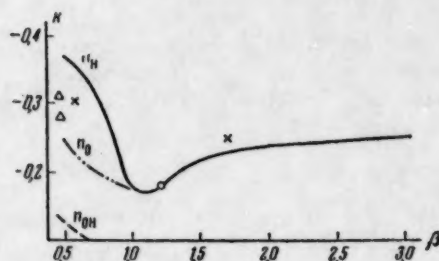


Fig. 3. The relation of exponent \underline{k} to β in a relation of the type $u_0 \sim P_{\Sigma}^{\underline{k}}$ for ethylene-air mixtures.

Fig. 3 shows the values of \underline{k} determined experimentally for an ethylene-air mixture: on a flat flame burner (triangles) [5], by a pipe method (crosses), and Gilbert's results (circles) [7]. It shows that the agreement between theoretical and experimental data is satisfactory.

The curve in Fig. 3 explains the increase in exponent \underline{k} observed experimentally [5] for propane-air and propylene-air mixtures with a change from lean to rich mixtures (for propane from $\underline{k} = -0.36$ at $\beta = 0.715$ to $\underline{k} = -0.10$ at $\beta = 0.955$, and for propylene from $\underline{k} = -0.25$ at $\beta = 0.675$, to $\underline{k} = -0.17$ at $\beta = 1.8$). In the region of lean mixtures, Fig. 3 gives sections for the composition dependences of exponent \underline{k} , calculated according to (3), with the assumption that the decisive role in the pressure dependence of u_0 is played only by oxygen atoms (n_O) or only by hydroxyl (n_{OH}). The data in Figs. 1 and 2 indicate that in the region of rich mixtures OH will give an exponent \underline{k} equal to -0.25 and the O atom, -0.50 . Each of the three active centers gives an increased \underline{k} close to the stoichiometric compositions. The slope of the curves of the pressure dependences of concentration and temperatures (Figs. 1 and 2) does not remain constant with a change in pressure for any mixture composition; the exponent \underline{k} increases in all cases when pressure falls as the rate of concentration growth decreases and the rate of fall in the combustion temperature increases. For this reason in all cases the theoretical values of \underline{k} are calculated above as the mean for the given range of pressure changes.

Fig. 4 gives the pressure dependences of concentration and temperatures T_r' with $\beta = 1.1$ for ethylene-air mixtures at various starting temperatures T_0 . With an increase in T_0 there will be an increase in exponent \underline{k} for a mixture of a given composition. The effect of an increase in T_0 is similar to an increase in the calorific value of the mixture of a given composition.

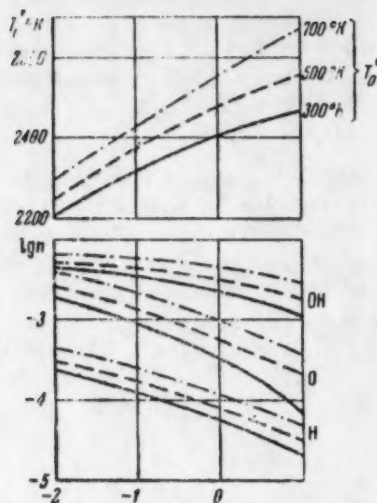


Fig. 4. Pressure dependences of H, O, and OH concentrations and combustion temperatures T_b for an ethylene-air mixture with an excess fuel coefficient $\beta = 1.1$ and at various values of T_0 .

which the most indefinite theoretical values of exponent k are possible, due to ignorance of the oxidation mechanism at high temperatures and the low H atom concentration (Fig. 1). The theoretical relation of exponent k to mixture composition, calorific value, and initial temperature will be further refined after the publication of the theory on chain-thermal flame propagation with two and three active centers. On the other hand, a refinement of the experimental pressure dependences of u_0 and a more detailed study of their relation to composition and initial conditions are required.

Temperature dependence of the flame propagation velocity.

The temperature dependence of u_0 is determined by relation (3). The initial temperature T_0 will have an effect mainly due to the change in the term including the ratio of the active center concentrations. This effect will be greatest for lean and rich mixtures, as, with a high calorific value, the combustion temperature will increase much more slowly than T_0 due to the sharp increase in the degree of dissociation at combustion temperatures above 2000°K. For the same reason, the rate of the u_0 increase will fall as the initial heating of a mixture of given composition increases (rise in T_0).

The ratio of the active center concentration is calculated by formula (4), with the use of (6) and (7), if there are no accurate data on composition. However, in this case, we should consider the fact already noted above that the actual value of the heat effect included in (7) may be used for complexly dissociated mixtures, for example, in converting atomic hydrogen concentrations for rich mixtures only. Fig. 5 shows the relations of the logarithms of the H, O, and OH concentrations to reciprocal temperature for mixtures of hydrocarbons of the C_nH_{2n} type with air. The slope for a given value of β determines a certain effective value of the heat of the H reaction if the square root of the concentration relation is written in the following form:

$$\sqrt{\frac{n_{rL}}{n_{rH}}} = \exp \left[\frac{H_i}{R} \left(\frac{1}{T_{rH}} - \frac{1}{T_{rL}} \right) \right]. \quad (9)$$

The flame propagation velocity in a methane-oxygen mixture of stoichiometric composition [6] does not depend on pressure ($k = 0$). However, a pressure dependence was established in [6] ($k = -0.05$) for a lean methane-oxygen mixture with a composition $CH_4 + 4O_2$. The lack of data on the concentrations of this mixture make it impossible to calculate the theoretical value of exponent k , but it follows from relation (3) that if u_0 is independent of pressure for a stoichiometric mixture then for lean and rich methane-oxygen mixtures u_0 should increase with a fall in pressure. The general character of the relation of k to β shown in Fig. 3 for an air mixture is the same for oxygen mixtures. However, in this case the region where k is large extends further to the right and left of $\beta = 1$, while for mixtures with low and high values of β the exponent value is close to -0.25 , as at these values of β the combustion temperature will be practically independent of pressure. Apparently, a positive value of the exponent, $k > 0$ (u_0 increases with pressure) is possible for fuel mixtures with very high calorific value or with a high initial temperature.

We cannot claim a high degree of accuracy for the theoretical results given as, the theoretical relation (3) was derived for a simplified chain reaction scheme with one active center [1]; however, it is apparent that they are not merely qualitative even for the region of lean mixtures for

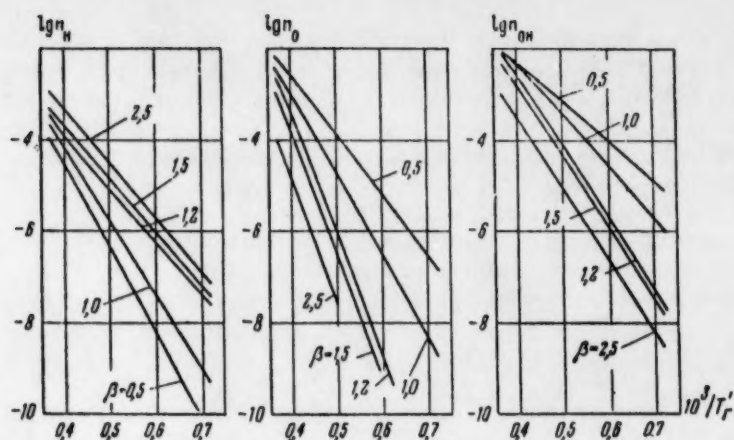


Fig. 5. Relation of the H, O, and OH concentrations (in g/g of mixture) to the reciprocal temperature (in °K) for C_nH_{2n} + air mixtures.

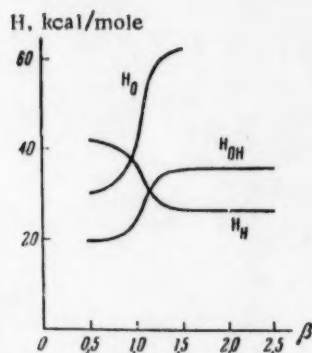


Fig. 6. The dependence of the effective heat H_i [formula(9)] on β for H, O, and OH.

Fig. 6 gives values for H_i at different values of β calculated by (9) on the basis of data in Fig. 5. It can be seen that there is a sharp change in H_i only in the region close to stoichiometric composition ($\beta = 1$).

If the concentration ratio from (9) is substituted in (3), it is then apparent that the slope of the curve of the relation between u_0 and the reciprocal combustion temperature is determined not only by the activation energy E , but also by the effective heat of reaction H_i of the leading active center. Therefore, in analyzing experimental data using formulas derived without consideration for the diffusion of the active center, instead of the activation energy E , a certain value, E_f , will be found, which will be approximately equal to the sum of activation energy E and the effective heat H_i , $E_f = E + H_i$, and, as relation (3) and data in Figs. 5 and 6 show, this value will depend on the starting composition of the fuel mixture and the initial temperature T_0^* at the given value of β .

SUMMARY

1. A relation was obtained for the pressure and temperature dependences of the flame propagation velocity from which it follows that the rate with which the flame propagation velocity changes with pressure depends on the composition of the fuel mixture and its calorific value, as well as on the initial temperature. In mixtures with high calorific value the flame propagation velocity may be independent of pressure.
2. The theoretical pressure dependences of the flame propagation velocity for a stoichiometric methane-air mixture and for ethylene-air mixtures of different compositions calculated by the given relation agree well with experimental data.
3. The slope of the graph of the relation of the flame propagation velocity logarithm to the reciprocal combustion temperature depends not only on the activation energy, but also on the heat of formation of the active center. The relation obtained makes it possible to find the true activation energy by analyzing experimental data.

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SYNTHESIS OF 15-HYDROXPENTADECANOIC AND 16-HYDROXYHEXADECANOIC ACIDS

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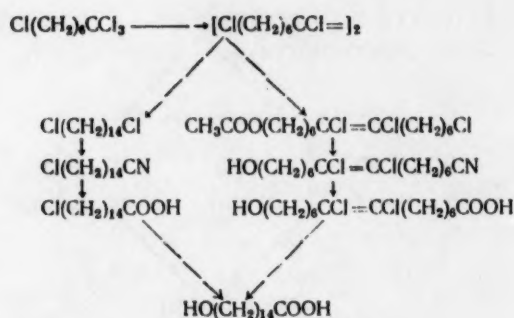
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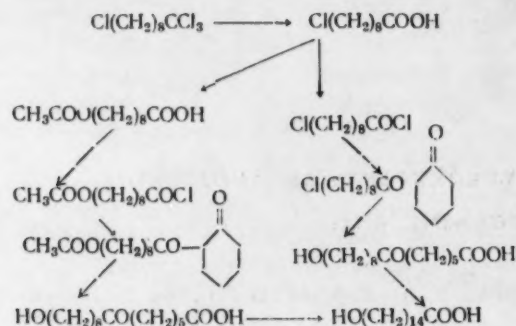
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$\alpha, \alpha, \alpha, \omega$ -Tetrachloroalkanes $\text{CCl}_3(\text{CH}_2\text{CH}_2)_n\text{Cl}$, which are obtained by the telomerization of ethylene with carbon tetrachloride, present great possibilities for the synthesis of various higher α, ω -bifunctional compounds. We have previously [1] synthesized dodecanedioic and hexadecanedioic acids from 1,1,1,5-tetrachloropentane and 1,1,1,7-tetrachloroheptane respectively. In the present work we investigated several ways of proceeding from 1,1,1,7-tetrachloroheptane and 1,1,1,9-tetrachlorononane to the synthesis of 15-hydroxypentadecanoic and 16-hydroxyhexadecanoic acids, which are of great interest because of the value of their lactones in perfumery (tibettolide, dihydroambrettolide). 15-Hydroxypentadecanoic acid was prepared from 1,1,1,7-tetrachloroheptane in accordance with the schemes:



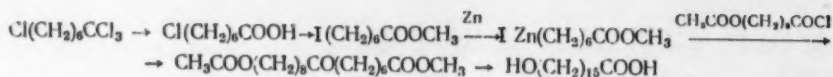
1,1,1,7-Tetrachloroheptane was hydrogenated in presence of Pd/BaSO_4 and ammonia to 1,7,8,14-tetrachloro-7-tetradecene or 1,14-dichlorotetradecane in the way which we have described previously [1]. Treatment of 1,14-dichlorotetradecane with sodium cyanide in 2-ethoxyethanol gave a mixture of the original compound, the mononitrile, and a little of the dinitrile, which was subjected to acid hydrolysis without prior separation. The resulting 15-chloropentadecanoic acid gave 15-hydroxypentadecanoic acid when heated in an autoclave with aqueous alkali. In accordance with the second scheme, 1,7,8,14-tetrachloro-7-tetradecene was converted into the monoacetoxyc compound, and alcoholysis of this and treatment with sodium cyanide gave 8,9-dichloro-15-hydroxy-8-pentadecenitrile. Hydrolysis of the nitrile group and hydrogenation over Raney nickel gave 15-hydroxypentadecanoic acid. By the first method the yield of 15-hydroxypentadecanoic acid was about 45% (on 1,14-dichlorotetradecene), and by the second method it was 36.3% (on 1,7,8,14-tetrachloro-7-tetradecene).

From 1,1,1,9-tetrachlorononane, 15-hydroxypentadecanoic acid was synthesized as follows:

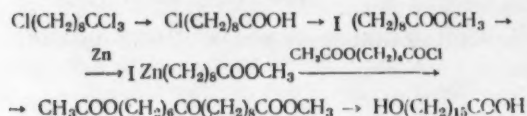


By hydrolysis with concentrated sulfuric acid, 1,1,1,9-tetrachlorononane was converted into 9-chlorononanoic acid. In accordance with the first scheme this was converted into 9-acetoxynonanoic acid, which was further converted into its acid chloride with thionyl chloride. 9-Acetoxynonanoyl chloride was brought into reaction with 1-(1-cyclohexen-1-yl) piperidine, as described for other acid chlorides [2]. Without being purified, the resulting diketone was subjected to alkaline scission, and without being isolated the keto acid was subjected to Kizhner reduction with hydrazine to 15-hydroxypentadecanoic acid. In accordance with the second scheme, analogous reactions were carried out with 9-chlorononanoyl chloride, but in this case the 15-chloro-7-oxopentadecanoic acid obtained after alkaline scission of the diketone was without isolation, subjected to alkaline hydrolysis to the corresponding hydroxy keto acid, which was then reduced with hydrazine. The yields of 15-hydroxypentadecanoic acid were about 75% (on 9-acetoxynonanoic acid) and about 60% (on 9-chlorononanoyl chloride).

The synthesis of 16-hydroxyhexadecanoic acid from 1,1,1,7-tetrachloroheptane and from 1,1,1,9-tetrachlorononane was carried out as follows:



and



In the first scheme the starting compounds are methyl 7-iodoheptanoate and 9-acetoxynonanoyl chloride; in the second scheme they are methyl 9-iodononanoate and 7-acetoxiheptanoyl chloride. All these are readily prepared from the corresponding ω -chloro carboxylic acids. These ω -iodo carboxylic esters were converted into the corresponding zinc derivatives by the action of zinc in accordance with the method developed previously [3]. By reaction with ω -acetoxy acid chlorides the zinc derivatives gave 16-acetoxy-8(or 10)-oxohexadecanoic esters, whose reduction with hydrazine led directly to 16-hydroxyhexadecanoic acid. The yields of 15-hydroxyhexadecanoic acid were about 50% by the first scheme and about 60% by the second scheme (on the corresponding ω -acetoxy acid chlorides).

EXPERIMENTAL

15-Chloropentadecanoic Acid. A mixture of 29 g of 1,14-dichlorotetradecane and 4.5 g of sodium cyanide in 60 ml of 2-ethoxyethanol was heated with stirring for four hours at 105-108°. The cooled reaction mixture was diluted with water and extracted with chloroform. After removal of solvent a solid residue remained. It was not

found possible to separate the mixture of products by vacuum distillation (b.p. 148-200°/1 mm). A solution of the mixture of products in acetic and hydrochloric acids was boiled for 16 hours, diluted with water, and extracted with chloroform. The chloroform extract was washed several times with dilute potassium hydroxide solution. On acidification of the alkaline solution there was a precipitate of mono- and dicarboxylic acids, which was recrystallized from petroleum ether. This gave 8.1 g of 15-chloropentadecanoic acid, m.p. 62-63°, undepressed by admixture of a known sample [4]. From the chloroform solution were recovered 12.5 g of 1,14-dichlorotetradecane.

Alkaline Hydrolysis of 15-Chloropentadecanoic Acid. A solution of 5.3 g of 15-chloropentadecanoic acid and 3.7 g of potassium hydroxide in 100 ml of water was heated in an autoclave at 150° for five hours. Acidification gave a precipitate of 15-hydroxypentadecanoic acid; yield 4.7 g; m.p. 82-83° (from benzene) [5, 6].

7,8,14-Trichloro-7-tetradecen-1-ol Acetic Ester. A mixture of 16.7 g of 1,7,8,14-tetrachloro-7-tetradecene, 19.6 g of anhydrous potassium acetate, and 100 ml of acetic acid was heated for 18 hours. The reaction mixture was treated with three times its volume of water and extracted with chloroform. Removal of solvent left 16.0 g (90%) of 7,8,14-trichloro-7-tetradecen-1-ol acetic ester; b.p. 181-183°/2 mm; n_D^{20} 1.4830; d_4^{20} 1.1132; found MR 91.81; calculated MR 91.88. Found: C 54.00; 53.97; H 7.83; 7.73%. $C_{14}H_{25}Cl_3O$. Calculated: $C_{16}H_{27}Cl_3O_2$. Calculated: C 53.71; H 7.60%.

7,8,14-Trichloro-7-tetradecen-1-ol. A mixture of 20.3 g of the acetic ester of 7,8,14-trichloro-7-tetradecen-1-ol, 50 ml of methanol, and 0.5 ml of concentrated hydrochloric acid was heated for six hours. Methanol and methyl acetate were distilled off, a further 50 ml of methanol and 0.5 ml of concentrated hydrochloric acid was added, and the mixture was heated for five hours. Methanol was distilled off, and the mixture was treated with water and chloroform. The chloroform solution was dried, and removal of chloroform gave 15.0 g (95%) of 7,8,14-trichloro-7-tetradecen-1-ol b.p. 178°/2 mm; n_D^{20} 1.4990; d_4^{20} 1.1231; found 82.49; calculated MR 82.51; Found: C 53.43; 53.31; H 7.86; 7.57%. $C_{14}H_{25}Cl_3O$. Calculated C 53.26; H 7.98%.

8,9-Dichloro-15-hydroxy-8-pentadecenitrile. A mixture of 27.3 g of 7,8,14-trichloro-7-tetradecen-1-ol, 126 g of sodium cyanide, 0.5 g of potassium iodide, 25 ml of water, and 100 ml of 2-ethoxyethanol was heated at 100° for six hours. The reaction mixture was treated with water and extracted with chloroform. After drying and removal of solvent we obtained 22 g (83%) of 8,9-dichloro-15-hydroxy-8-pentadecenitrile; b.p. 205°/2 mm; n_D^{20} 1.4910; d_4^{20} 1.0803; found MR 82.14; $C_{15}H_{25}Cl_2NO$. Calculated MR 82.08.

8,9-Dichloro-15-hydroxy-8-pentadecenoic Acid. A mixture of 22 g of 8,9-dichloro-15-hydroxy-8-pentadecenitrile, 25 ml of hydrochloric acid, and 25 ml of glacial acetic acid was heated for six hours. The reaction mixture was treated with excess of water and extracted with chloroform. The solution was dried, and removal of chloroform gave 18.4 g (80%) of 8,9-dichloro-15-hydroxy-8-pentadecenoic acid; b.p. 210°/1 mm; n_D^{20} 1.4865; d_4^{20} 1.1074; found MR 84.44; calculated MR 84.48. Found: C 55.32; 55.64; H 7.89; 7.84; Cl 21.61; 21.75%. $C_{15}H_{26}Cl_2O_3$. Calculated: C 55.37; H 8.05; Cl 21.79%.

15-Hydroxypentadecanoic Acid. 8,9-Dichloro-15-hydroxy-8-pentadecenoic acid (9.0 g) was dissolved in aqueous alkali (8.4 g of potassium hydroxide in 300 ml of water) and hydrogenated in the presence of 3g of Ni catalyst for six hours at 100 atm and 100°. The catalyst was filtered off, and the filtrate was acidified with hydrochloric acid. This gave 3.9 g (54.9%) of 15-hydroxypentadecanoic acid, m.p. 78° (from benzene + petroleum ether).

15-Hydroxypentadecanoic Acid from 9-Chlorononanoic Acid. a) A solution of 56 g of 9-chlorononanoic acid and 57 g of potassium hydroxide in 275 ml of water was heated in an autoclave at 150° for five hours. When cool, the solution was acidified with dilute sulfuric acid. The precipitated 9-hydroxynonanoic acid was extracted with ether. The ether solution was dried over magnesium sulfate. Ether was removed, and 35 g of acetic anhydride was added to the residue. Reaction occurred with evolution of heat. The mixture was boiled for ten minutes, and vacuum distillation then gave 43.4 g of 9-acetoxynonanoic acid (b.p. 158-160°/2 mm; n_D^{20} 1.4462; d_4^{20} 1.0518) and 6.7 g of residue, which on hydrolysis with sodium hydroxide solution gave 5.1 g of 9-hydroxynonanoic acid. The 43.4 g of 9-acetoxynonanoic acid was heated with 50 ml of thionyl chloride for four hours. Distillation gave 43 g of 9-acetoxynonanoyl chloride, b.p. 125-126°/2 mm. A solution of this 43 g of acid chloride in 60 ml of chloroform was added over a period of 30 minutes to a stirred solution of 35 g of 1-(1-cyclohexen-1-yl) piperidine* and 24 g of triethylamine in 200 ml of dry chloroform at 35°. The mixture was stirred at this temperature

*Hunig and co-workers [2] state that they obtained a yield of 55% in the preparation of 1-(1-cyclohexen-1-yl) piperidine from cyclohexanone and piperidine. We found that the yield could be raised to 70-75% by increase in the reaction time.

for one hour and then left for 12 hours. A solution of 50 g of concentrated sulfuric acid in 70 ml of water was added, and the reaction mixture was boiled with stirring for four hours. The chloroform solution was separated, washed with water, and dried over magnesium sulfate. Removal of chloroform left 53.4 g of residue. The residue was heated to 100° and added with stirring to a solution of 47 g of potassium hydroxide in 33 ml of water at 100°. In the course of this the temperature rose to 123°, and the reaction mixture was stirred for ten minutes at this temperature. A small part of the mixture was dissolved in hot water and acidified with dilute sulfuric acid. The precipitate formed was dissolved in chloroform. The chloroform solution yielded 15-hydroxy-7-oxopentadecanoic acid, m.p. 82-83° (from benzene). Found: C 66.15; 66.00; H 10.16; 10.34%. $C_{15}H_{28}O_4$. Calculated: C 66.17; H 10.29%.

To the hot mass we added 150 ml of diethylene glycol and 70 ml of hydrazine hydrate. The solution was boiled for eight hours, after which 24 g of potassium hydroxide in 100 ml of diethylene glycol was added; water and excess of hydrazine hydrate were distilled from the mixture until the temperature in the liquid reached 195°. The reaction mixture was then boiled for 15 hours. The hot solution was poured into 1 liter of hot water and acidified with dilute sulfuric acid. The precipitated 15-hydroxypentadecanoic acid was filtered off, washed with water, and dried. We obtained 38.5 g of substance, m.p. 84.85° (from benzene).

b) From 26.8 g of 9-chlorononanoyl chloride, 23 g of 1-(1-cyclohexen-1-yl) piperidine, and 15.5 g of triethylamine we obtained, after hydrolysis, 30 g of diketone; b.p. 178-180°/2 mm; n_D^{20} 1.5065. Found: C 66.17; 66.24; H 9.18; 9.32%. $C_{15}H_{26}ClO_2$. Calculated: C 66.06; H 9.17%.

This 30 g of diketone was treated with 26 g of potassium hydroxide in 18 ml of water, as described above, for 20 minutes. The hot mixture was then poured into hot water to make a total volume of 350 ml and was heated in an autoclave at 145-155° for five hours. The cooled solution was extracted with ether and acidified with dilute sulfuric acid. The precipitate formed was extracted with chloroform. We obtained 23.8 g of 15-hydroxy-7-oxopentadecanoic acid, m.p. 82-83° (from benzene), undepressed by admixture of the sample from the preceding experiment. Reduction similar to that described above gave 18.4 g of 15-hydroxypentadecanoic acid.

Methyl 7-Iodoheptanoate. A solution of 44.3 g of methyl 7-chloroheptanoate [4] and 55.8 g of sodium iodide in 300 ml of acetone was boiled for 12 hours. We obtained 58.8 g of the methyl ester; b.p. 107-109°/3 mm; n_D^{20} 1.4958; d_4^{20} 1.4672; found MR 53.74; calculated MR 53.60. Found: C 35.74; 35.70; H 5.71, 5.69%. $C_8H_{15}IO_2$. Calculated: C 35.55; H 5.55%.

Methyl 16-Acetoxy-8-oxohexadecanoate. A mixture of 47.8 g of methyl-7-iodoheptanoate, 19 g of zinc dust (previously treated with copper sulfate solution and dried), 2 ml of ethyl acetate, and 30 ml of dry toluene was boiled with stirring for three hours. The mixture was cooled, and over a period of 30 minutes a solution of 31.2 g of 9-acetoxynonanoyl chloride in 40 ml of toluene was added. On the next day the reaction mixture was heated with stirring for ten minutes in a water bath, cooled, diluted with benzene, and filtered from excess of zinc. The filtrate was washed with dilute sulfuric acid, water, and sodium carbonate solution and was dried over calcium chloride. Solvent was distilled off, and vacuum distillation gave 7.1 g of methyl heptanoate and 23.2 g (51%) of methyl 16-acetoxy-8-oxohexadecanoate; b.p. 209-211°/2 mm; m.p. 52-53° (from petroleum ether). Found: C 66.73; 66.79; H 10.26; 10.28%. $C_{19}H_{34}O_5$. Calculated: C 66.70; H 9.96%.

16-Hydroxyhexadecanoic Acid. A solution of 7.1 g of methyl 16-acetoxy-8-oxohexadecanoate in 15 ml of diethylene glycol was added to a solution of 2.9 g of potassium hydroxide in 20 ml of diethylene glycol. The mixture was heated at 120-130° without a condenser for 20 minutes, 8 ml of hydrazine was added, and the reaction mixture was boiled for eight hours. Addition was made of 7.5 g of potassium hydroxide in 20 ml of diethylene glycol. Water and excess of hydrazine hydrate were distilled off until the temperature in the liquid reached 195°. The solution was boiled for 15 hours and then poured into hot water and acidified with dilute sulfuric acid. We obtained 5.3 g of 16-hydroxyhexadecanoic acid, m.p. 93-94° (from benzene).

7-Acetoxyheptanoyl Chloride. A solution of 45 g of 7-chloroheptanoic acid and 35 g of sodium hydroxide in 250 ml of water was heated in an autoclave at 150° for four hours. The solution was acidified with dilute sulfuric acid, and the 7-hydroxyheptanoic acid was extracted with ether and dried over magnesium sulfate. Ether was removed, and 34 g of acetic anhydride was added to the residue. Reaction occurred with evolution of heat. The solution was boiled for ten minutes and vacuum-distilled. We obtained 39.1 g of 7-acetoxyheptanoic acid;

b.p. 142-143°/2 mm; n_D^{20} 1.4420; d_4^{20} 1.0570; found MR 47.06; calculated MR 46.95. On alkaline hydrolysis the residue gave 5.1 g of 7-hydroxyheptanoic acid. A mixture of 32 g of 7-acetoxyheptanoic acid and 40 ml of thionyl chloride was heated for four hours. We obtained 31.3 g of 7-acetoxyheptanoylchloride, b.p. 106-107°/2 mm.

Methyl 9-Iodononanoate. A solution of 35.2 g of methyl 9-chlorononanoate [4] and 49 g of sodium iodide in 260 ml of acetone was heated in a water bath for 16 hours. We obtained 43.2 g (87%) of methyl 9-iodononanoate; b.p. 124-127°/2 mm; n_D^{20} 1.4911; d_4^{20} 1.3730; found MR 63.09; calculated MR 62.84. Found: C 40.44; 40.51; H 6.50; 6.42%, $C_{19}H_{35}IO_2$. Calculated: C 40.26; H 6.37%.

Methyl 16-Acetoxy-10-oxohexadecanoate. The procedure was analogous to that of the experiment with methyl 7-iodoheptanoate: From 41 g of methyl 9-iodononanoate, 14 g of zinc, and 21.5 g of 7-acetoxyheptanoyl chloride we obtained 5.1 g of methyl nonanoate and 22.4 g (62.5%) of methyl 16-acetoxy-10-oxodecanoate; b.p. 205-207°/2 mm; m.p. 40.41° (from petroleum ether). Found: C 66.40; 66.53; H 10.14; 10.05%. $C_{19}H_{34}O_5$. Calculated: C 66.70; H 9.96%.

Reduction of this keto ester with hydrazine hydrate gave 16-hydroxyhexadecanoic acid in 92.4% yield.

SUMMARY

1. 15-Hydroxypentadecanoic acid was synthesized by several routes from 1,1,1,7-tetrachloroheptane and 1,1,1,9-tetrachlorononane.
2. 16-Hydroxyhexadecanoic acid was synthesized from 1,1,1,7-tetrachloroheptane and 1,1,1,9-tetrachlorononane via the corresponding ω -chloro carboxylic acids.

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*Original Russian pagination. See C. B. translation.

PREPARATION AND PROPERTIES OF 2-MERCURATED PHENYLACETALDEHYDE

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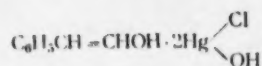
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The first reference to the reaction between mercuric acetate and a vinyl ether, namely ethyl styryl ether, is met in a paper of Manchot in 1918 [1]. In view of the fact that the conditions under which Manchot carried out the reaction were substantially different from those developed by us and the compound which he obtained was greatly different in properties from mercurated aldehydes, we have also studied the reaction of ethyl styryl ether with mercury salts.

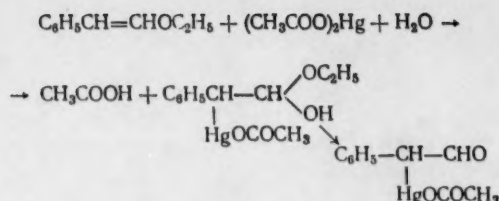
The reaction was carried out by Manchot as follows: Ethyl styryl ether was heated with an aqueous solution of mercuric acetate at 50° for two hours. Three moles of mercury salt were taken to each mole of styryl ether. The cooled reaction mixture was poured into a 10% solution of common salt; a white precipitate of the mercury compound was formed. Mainly on the basis of the results of analysis, Manchot, in accordance with his views on the complex nature of the products of reaction between unsaturated compounds and mercury salts, proposed the following structure for the mercury derivative prepared in this way:



The yield of mercury compound, calculated on the basis of the proposed formula, was about 85%.

Before passing to a critical examination of the experimental procedure and Manchot's conclusions, we shall give the properties and reactions of the product on the basis of which the author proposed the structure as a complex of styryl alcohol and basic mercury salt. When heated in a capillary the substance melted partially at 120°; it was insoluble in water and dilute acetic acid; it was extremely sparingly soluble in alcohol and organic solvents. If the organomercury compound was boiled with hydrochloric acid and then steam-distilled, apart from some phenylacetaldehyde a little of a substance that solidified in the condenser came over; the solid substance melted at about 80°. The bulk of the organic substance remained in the distillation flask as a mercury-containing resin. The formation of phenylacetaldehyde in the decomposition of the organomercury compound was proved by its conversion into the oxime. As regards the solid product which separated during the decomposition of the mercury compound with hydrochloric acid, Manchot makes no further reference to it. These few experiments already give convincing proof that Manchot was dealing not with an individual compound, but with a mixture of substances. The solid compound of m.p. about 80° obtained in the decomposition of the mercury-containing product with acid, which Manchot did not investigate further, was undoubtedly phenylacetic acid, for which the literature gives m.p. 77.5-78° [3] and m.p. 78° [4].

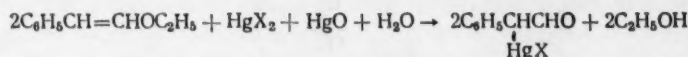
The formation of phenylacetic acid can be readily explained as follows. The reaction of the styryl ether with the first molecular proportion of mercuric acetate must proceed rapidly in the cold with formation of monomercurated phenylacetaldehyde:



In this way cleavage of the styryl ether occurs and a compound with a free aldehyde group is formed. The action of the other two molecular proportions of mercuric acetate may go in two directions: further mercuriation of the mercury derivative, which requires more severe conditions than the addition reaction (these conditions were to some extent achieved in Manchot's experiments), and oxidation of the aldehyde group by the mercuric salt, which will give mercurated phenylacetic acid. Under the conditions described by Manchot, this last compound could be mercurated further. Mercurated phenylacetic acid could also form an internal salt. It is known that both polymercurated compounds and internal salts of mercurated carboxylic acids are usually almost completely insoluble in organic solvents. This is what Manchot actually found for the mercury-containing product that he isolated in the reaction. Hence, we have shown that the conditions of the experiment were such that the product would be a mixture of mercurated substances of various structures. The action of hydrochloric acid on such a mixture should, after the elimination of mercury, lead to a mixture of phenylacetaldehyde and phenylacetic acid. The first of these substances was isolated and characterized by Manchot, the second was probably obtained, but was disregarded.

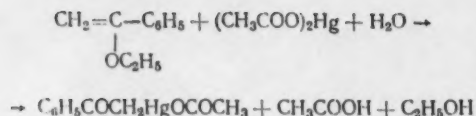
We have also carried out a reaction between ether styryl ether and mercuric acetate. However, in accordance with the method which we have developed for the preparation of monomercurated aldehydes, we took the reactants in equimolecular proportions and carried out the reaction in the cold, which enabled us to avoid subjecting the aldehyde group to the action of an oxidizing agent (mercuric salt). Reaction went rapidly in the cold, and the (acetoxymercuri)-phenylacetaldehyde was precipitated as a heavy oil, which did not crystallize on standing. When the (acetoxymercuri)-phenylacetaldehyde was dissolved in alcohol, polymerization appeared to set in after a few hours (this is characteristic also for phenylacetaldehyde itself), and it was precipitated as a solid, insoluble in the usual organic solvents.

The position of the mercury atom-linked to a carbon which is attached both to a carbonyl group and to a phenyl group-makes it extremely sensitive to the action of a halide. Thus, if (acetoxymercuri)-phenylacetaldehyde is dissolved in aqueous acetone and aqueous potassium chloride is added with the object of obtaining (chloromercuri)-phenylacetaldehyde, the C-Hg bond is hydrolyzed and phenylacetaldehyde is liberated; since alkali is liberated at the same time, amorphous insoluble precipitates are formed from the mercuric salt and phenylacetaldehyde. We observed similar behavior in the cleavage of a C-Hg bond in mercuridiacetaldehyde with an aqueous solution of potassium chloride. We succeeded in obtaining (chloromercuri)- and (bromomercuri)-acetaldehydes as excellently formed crystals by the reaction of ethyl styryl ether with an equimolecular mixture of mercuric halide and mercuric oxide in aqueous acetone:



The (halomercuri)-acetaldehydes obtained are crystalline compounds, readily soluble in alcohol and acetone and crystallizable from dichloroethane; when heated quickly they melt sharply, but above this they solidify again and cannot be remelted; this is probably due to polymerization. The analyses for mercury were somewhat high (about 1%), which is associated with the difficulty in purifying the precipitate of mercury sulfide from the phenylacetaldehyde polymer formed under the conditions applying during the decomposition of the sample. The elementary analysis of the substances for C and H showed that pure compounds had been obtained.

Ethyl 1-phenylvinyl ether, and also α -acetoxystyrene, reacted smoothly with mercuric acetate with formation of 2-(acetoxymercuri)-acetophenone:



The chloride prepared from it had the same melting point as the compound described by Dimroth, which he synthesized by direct mercuriation of acetophenone [5].

EXPERIMENTAL

Reaction of Mercuric Acetate with Ethyl Styryl Ether. Ethyl styryl ether (3 g; 0.02 mole) was added to a solution of 6.4 g (0.02 mole) of mercuric acetate in 20 ml of water. The addition reaction of the mercury salt was accompanied by evolution of heat, and a mercury compound was precipitated as a heavy noncrystallizing oil. The aqueous part was separated, and the oil was dissolved in 25 ml of alcohol. After 12 hours there formed a precipitate of mercury-containing polymer, insoluble in the usual solvents.

Preparation of (Chloromercuri)-phenylacetaldehyde. A solution of 1.35 g (0.005 mole) of mercuric chloride in 8 ml of acetone was added to a mixture of 1.5 g (0.01 mole) of ethyl styryl ether, 1.1 g (0.005 mole) of mercuric oxide, 5 ml of acetone, and 1 ml of water. The reaction mixture was heated to the boil and quickly filtered. The filtrate was cooled, and part of the acetone was evaporated off; crystals of (chloromercuri)-phenylacetaldehyde separated and were washed with a little cooled acetone and dry ether. Yield 3.2 g (88%); m.p. 121-123°. (Chloromercuri)-phenylacetaldehyde is soluble in alcohol, acetone, and chloroform. Found: C 27.36; 27.44; H 2.13; 2.01; Hg 56.98%. $\text{ClHgCH}(\text{C}_6\text{H}_5)\text{CHO}$. Calculated: C 27.03; H 1.98; Hg 56.48%.

Preparation of (Bromomercuri)-phenylacetaldehyde. In a similar way, a solution of 1.8 g (0.005 mole) of mercuric bromide in 10 ml of acetone was added to a mixture of 1.5 g (0.01 mole) of ethyl styryl ether, 1.1 g (0.005 mole) of mercuric oxide, 7 ml of acetone, and 1 ml of water. After a short boil, filtration, and partial removal of acetone, crystals of (bromomercuri)-phenylacetaldehyde separated. Yield 2.2 g (55%); m.p. 116-117° (from dichloroethane). (Bromomercuri)-phenylacetaldehyde is soluble in alcohol, acetone, and dichloroethane. Found: C 24.19; 24.06; H 1.91, 1.90; Hg 51.29; 51.13%. $\text{BrHgCH}(\text{C}_6\text{H}_5)\text{CHO}$. Calculated: C 24.04; H 1.76; Hg 50.22%.

Reaction of Mercuric Acetate with Ethyl 1-Phenylvinyl Ether. Ethyl 1-phenylvinyl ether (3 g; 0.02 mole) was added to a solution of 6.4 g (0.02 mole) of mercuric acetate in 20 ml of water. The addition reaction of the mercury salt was rapid, and the organomercury compound was precipitated on the bottom of the flask as a heavy oil, which crystallized after several minutes. The 2-(acetoxymmercuri)-acetophenone was separated and washed with ether. Yield 6.5 g (86%); m.p. 112.5-113° (from benzene). Found: Hg 53.19; 52.79%. $\text{CH}_3\text{COOHgCH}_2\text{COC}_6\text{H}_5$. Calculated: Hg 52.96%.

Reaction of α -Acetoxystyrene with Mercuric Acetate. α -Acetoxystyrene (16.2 g; 0.1 mole) was added to 32 g (0.1 mole) of mercuric acetate in 100 ml of water. The addition reaction of the mercury salt went rapidly with evolution of heat. The 2-(acetoxymmercuri)-acetophenone, which was formed as an oil, rapidly crystallized. Yield 33.5 g (88%); m.p. 112.5-113° (from benzene). Found: C 31.65; 31.46; H 2.70; 2.71; Hg 52.83; 53.23%. $\text{CH}_3\text{COOHgCH}_2\text{COC}_6\text{H}_5$. Calculated: C 31.63; H 2.66; Hg 52.96%.

SUMMARY

A method is proposed for the synthesis of 2-monomercurated phenylacetaldehyde and acetophenone by the addition of mercuric salts to phenyl-substituted vinyl ethers and esters.

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REACTIONS OF FLUORO OLEFINS

COMMUNICATION 11. REACTIONS OF COMPOUNDS OF THE PERFLUOROISOBUTENE SERIES

WITH AMINES AND AMMONIA

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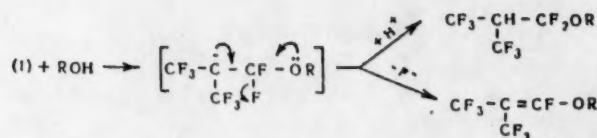
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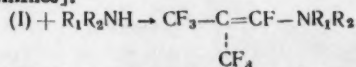
Original article submitted July 4, 1958

Perfluoroisobutene [pentafluoro-2-(trifluoromethyl) propene] $\text{CF}_3-\text{C}(\text{CF}_3)=\text{CF}_2$ (I) is a compound in which the

specific properties of fluoro olefins are most strongly manifested. Thus, we showed previously that, even in absence of alkaline catalysts, (I) readily reacts with alcohols and, apart from addition products, unsaturated ethers are formed which correspond in structure to the replacement of a vinyl fluorine atom of (I) by an alkoxy group [1]:



(I) reacts extremely vigorously with amines with exclusive formation of perfluoroisobutenylamines [tetrafluoro-2-(trifluoromethyl) propenylamines]:



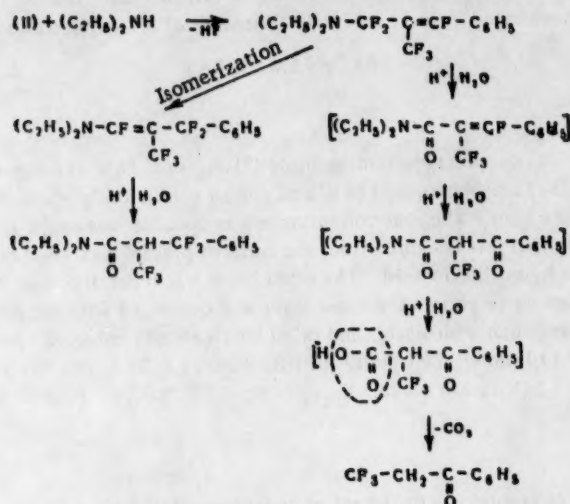
The high reactivity of (I) toward alcohols and amines is due to its very marked electrophilic character, which is caused by the powerful electron-attracting effect of two trifluoromethyl groups and also the lack of symmetry of the molecule. These properties enable us to obtain compounds in which a 1-fluorine of perfluoroisobutene is replaced by an alkoxy or dialkylamino group. We considered it to be of interest to study the character of the reaction of 1-alkyl- and 1-aryl-heptafluoroisobutenes with nucleophilic reagents, in particular with ammonia and amines. For the introduction of alkyl and aryl groups in the 1-position, in the present investigation we carried out reactions of (I) with Grignard reagents, which proceed as follows: $(I) + \text{RMgBr} \rightarrow \text{CF}_3-\underset{\text{CF}_3}{\text{C}}=\text{CF}-\text{R}$ This re-

action has already been carried out with other fluoro olefins by Tarrant and Warner [2].

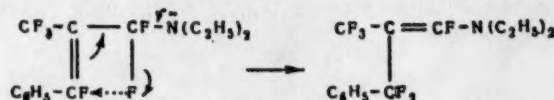
For the reactions of 1-alkyl- and 1-aryl-heptafluoroisobutenes with nucleophiles two probable courses can be suggested: 1) replacement of the vinyl fluorine atom; 2) attack at a trifluoromethyl group with replacement of an allyl fluorine atom, the mobility of which is due to hyperconjugation:



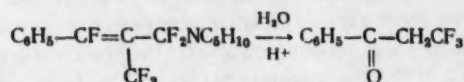
Hydrolysis of this mixture gives trifluoropropiophenone and N,N-diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl) propanamide. The most probable scheme of transformations is as follows:



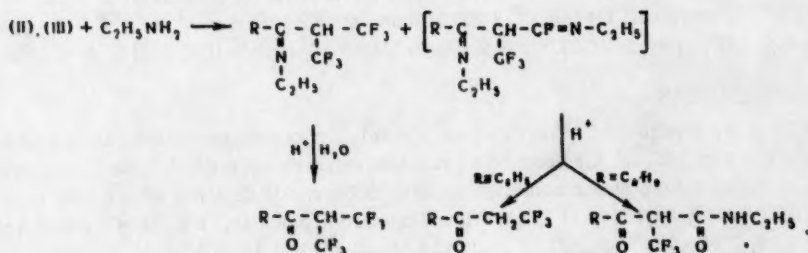
The mechanism of the isomerization is evidently analogous to that of the anionotropic rearrangement previously proposed by us for fluoropropenes [3]:



In the case of piperidine this rearrangement is not observed, and the acid hydrolysis of 1-[1,1,3-trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine leads only to 3,3,3-trifluoropropiophenone:



In its reactions with 1-substituted heptafluoroisobutenes, ethylamine occupies a position intermediate between ammonia and dialkylamines; as well as replacement of a vinyl fluorine atom, the fluorine of a trifluoromethyl group is replaced, which is confirmed by the isolation from the hydrolyzate of trifluoropropiophenone in the case of (II) and of $\text{C}_2\text{H}_5\text{NH}-\text{C}(\text{CF}_3)(\text{H})-\text{CH}(\text{CF}_3)-\text{C}_6\text{H}_5$ in the case of 1-butylheptafluoroisobutene (III):



In order to compare the reactivities of 1-substituted heptafluoroisobutenes with those of the corresponding compounds of the unbranched propene series, pentafluoro-1-phenylpropene was prepared by the action of phenylmagnesium bromide on hexafluoropropene; it was found that this substance did not react with amines and ammonia, but reacted with concentrated sulfuric acid with formation of 2,3,3,3-tetrafluoropropiophenone.

EXPERIMENTAL

Heptafluoro-1-phenylisobutene (II).

A solution of 0.2 mole of phenylmagnesium bromide (31.4 g of C_6H_5Br and 5 g of Mg) was prepared in the usual way in 300 ml of dry ether and was cooled to 0° and stirred continuously while 30 g (0.15 mole) of (I) was introduced over a period of one hour. The reaction mixture was then left overnight at room temperature. On the next morning the ethereal solution was decanted from the resinous precipitates and carefully poured into a mixture of crushed ice and dilute hydrochloric acid. The ether layer was separated, and the aqueous layer was extracted with three 150-ml portions of ether; the ether layer was combined with the ether extracts, washed with sodium bicarbonate solution and then with water, and dried over calcium chloride. Solvent was distilled off, and distillation then gave 30 g (0.116 mole; 77% yield) of (II); b.p. $75.5-76.5^\circ$ (45 mm); n_D^{20} 1.4275; d_4^{20} 1.3966; found MR 47.50; calculated $C_{10}H_5F_7$ MR 45.29. λ_{max} 6.90; 6.76; 5.95 μ . Found: C 46.27; H 2.17%. $C_{10}H_5F_7$. Calculated: C 46.52; H 1.95%.

Hydrolysis of (II).

A mixture of 6.6 g (0.0256 mole) of (II), 10 ml of concentrated sulfuric acid, and 0.5 g of silica gel was heated at $80-100^\circ$ for six hours with vigorous stirring. There was a vigorous evolution of hydrogen fluoride. When cool, the reaction mixture was extracted with methylene chloride (five 15-ml portions). The extract was washed with water and dried over magnesium sulfate. Solvent was distilled off, and the residue was vacuum-distilled. This gave 2.6 g (0.01 mole) of unchanged (II) (b.p. $75-78^\circ$; n_D^{20} 1.4280) and 1.7 g (42% on the olefin that reacted) of hexafluoroisobutyrophenone; m.p. $35.5-36^\circ$ (from octane); λ_{max} 6.29; 5.85 μ . Found: C 46.89; H 2.32; F 44.80%. $C_{10}F_6H_6O$. Calculated: C 46.88; H 2.36; F 44.50%.

Oxidation of (II).

Over a period of one hour 10 g (0.039 mole) of (II) was added dropwise to a stirred mixture of 100 ml of water and 30 g of potassium permanganate at $35-40^\circ$. During the addition, carbon dioxide was continuously passed through the reaction mixture. The mixture was then stirred further for 12 hours. The reaction mixture was then cooled to 0° , and sulfur dioxide was passed until the solution was decolorized. The mixture was extracted with ether in a continuous extractor for three days. The ether extract was dried over magnesium sulfate. Ether was carefully distilled off, and the residue was vacuum-distilled. This gave 4.9 g (68%) of hexafluoroacetone hydrate; b.p. $49-50^\circ$ (800 mm); n_D^{20} 1.3160. The literature [4] gives: b.p. $55-56^\circ$ (80 mm); n_D^{20} 1.3179. From the residue remaining after distillation of the liquid part we obtained 4.7 g (99%) of crystals of m.p. 119° (from water). A mixture with benzoic acid melted without depression (m.p. 120°).

Pentafluoro-1-phenylpropene.

Hexafluoropropene (30 g; 0.2 mole) was passed into a continuously stirred solution of 0.3 mole of phenylmagnesium bromide (47.1 g of C_6H_5Br and 8 g of Mg) in 300 ml of ether at room temperature. The reaction mixture was treated in the usual way. Fractionation gave 17 g (0.082 mole; 42% yield) of pentafluoro-1-phenylpropene; b.p. $77-78^\circ$ (65 mm); n_D^{20} 1.4482; d_4^{20} 1.3210; found MR 42.19, calculated for $C_9H_5F_5$ MR 40.39. The literature [5] gives b.p. 148° . Found: C 52.11; H 2.45%. $C_9H_5F_5$. Calculated: C 52.43; H 2.42%.

2,3,3,3-Tetrafluoropropiophenone.

A mixture of 10 g of pentafluoro-1-phenylpropene, 10 ml of concentrated sulfuric acid, and 5 g of silica gel powder was heated at $125-135^\circ$ for 3.5 hours. The reaction mixture was cooled, diluted with methylene chlorides, washed with water, and dried over magnesium sulfate. Solvent was distilled off, and the residue was vacuum-distilled. This gave 8.3 g (84%) of 2,3,3,3-tetrafluoropropiophenone; b.p. $41-42^\circ$ (from hexane). Found: C 52.71; H 2.86; F 36.82%. $C_9H_5F_4O$. Calculated: C 52.43; H 2.93; F 36.87%.

The 2,4-dinitrophenylhydrazone had m.p. $172.5-173.5^\circ$ (from alcohol). Found: N 14.72%. $C_{15}H_{10}F_4N_2O_4$. Calculated: N 14.50%.

1-2-Dibromopentafluoro-1-phenylpropane.

Pentafluoro-1-phenylpropene (5.9 g) was treated with excess of a solution of bromine in methylene chloride at 40°. This gave 7.6 g (74%) of 1,2-dibromopentafluoro-1-phenylpropane; b.p. 106-107° (22 mm); n_D^{20} 1.4993; d_4^{20} 1.9168; Found MR 55.43; calculated for $C_9H_5F_5Br_2$ MR 56.39. Found: C 29.02; H 1.44%. $C_9H_5F_5Br_2$. Calculated: C 29.37; H 1.37%.

1-Butylheptafluoroisobutene.

With vigorous stirring and cooling to 0°, 20 g (0.1 mole) of (I) was introduced into a solution of 0.2 mole of butylmagnesium bromide in 30 ml of ether. After four hours the mixture was treated in the usual way. This gave 16.3 g (70%) of (III); b.p. 113-114° (750 mm); m.p. -70°; n_D^{20} 1.3390; d_4^{20} 1.2769; found MR 38.99; calculated for $C_8H_9F_7$ MR 39.66; λ_{max} 5.88; 5.68 μ . Found: C 40.33; H 3.69%. $C_8H_9F_7$. Calculated C 40.34; H 3.81%.

Heptafluoro-1-styrylisobutene.

Excess of perfluoroisobutene was passed into a stirred solution of 0.1 mole of styrylmagnesium bromide (from 16.3 g of β -bromostyrene and 3 g of Mg) in 200 ml of ether at 0°. The mixture was then left for three days at room temperature. The ether solution was then separated from the resinous precipitate, either was distilled off, and the residue was vacuum-distilled. This gave 9.6 g (32%) of heptafluoro-1-styrylisobutene; b.p. 87-87.5° (12 mm); n_D^{20} 1.4852; d_4^{20} 1.3734. Found: C 50.54; H 2.46%. $C_{12}H_7F_7$. Calculated: C 50.71; H 2.48%.

1-Ethylheptafluoroisobutene.

With vigorous stirring and cooling to 0°, an excess of dry perfluoroisobutene was passed into a solution of 0.13 mole of ethylmagnesium bromide (from 14.2 g of C_2H_5Br and 4 g of Mg) in 150 ml of dibutyl ether. The mixture was left at room temperature for two days. The contents of the reaction flask were then poured into a mixture of dilute hydrochloric acid and ice. The aqueous layer was extracted with dibutyl ether, and the ether extracts were combined and dried over calcium chloride. A fraction of b.p. 44-135° was distilled from the dibutyl ether solution. Further fractionation of this through a column of 18-plate efficiency gave 15.3 g (56%) of 1-ethylheptafluoroisobutene; b.p. 73.5-74° (752 mm); n_D^{20} 1.3122; d_4^{20} 1.3548; found MR 30.08; $C_8H_9F_7$; calculated MR 30.42. Found: C 34.36; H 2.28%. $C_8H_9F_7$. Calculated: C 34.30; H 2.39%.

Heptafluoro-1-isopentylisobutene.

With stirring and cooling to 0°, 40 g (0.2 mole) of dry perfluoroisobutene was passed into a solution of 0.2 mole of isopentylmagnesium bromide (from 30.1 g of i - $C_5H_{11}Br$ and 5.2 g of Mg) in 150 ml of dry ether. After the usual treatment we obtained 27.8 g (55%) of heptafluoro-1-isopentylisobutene; b.p. 57° (58 mm); n_D^{20} 1.3500; d_4^{20} 1.2017; found MR 45.15; $C_9H_{11}F_7$; calculated MR 44.27. Found: C 43.34; H 4.60%. $C_9H_{11}F_7$. Calculated: C 42.86; H 4.40%.

Reactions of Heptafluoro-1-phenylisobutene.

Imine of Hexafluoroisobutyrophenone [α -[2,2,2-trifluoro-1-(trifluoromethyl) ethyl]benzylidenimine]. Dry ammonia was passed for one hour into a solution of 14.1 g (0.054 mole) of (II) in 200 ml of dry ether cooled to 0°. After one day the precipitate of NH_4F (2.45 g) was filtered off, ether was distilled off, and the residue was vacuum-distilled. This gave 10 g (72%) of the imine of hexafluoroisobutyrophenone, b.p. 74-75° (3 mm) and n_D^{20} 1.4600; a slightly yellowish liquid which decomposes when kept for a short time. Found: C 47.25; H 2.76; F 44.67%. $C_{10}H_7F_6N$. Calculated C 47.07; H 2.83; F 43.20%.

Hexafluoroisobutyrophenone. Concentrated hydrochloric acid (20 ml) was mixed with 5.6 g (0.022 mole) of the imine of hexafluoroisobutyrophenone. Heat was evolved and a precipitate formed. The mixture was boiled for 15 hours in a water bath and extracted with ether. The extract was dried, and ether was distilled off. The residue came over at 75-85° (11 mm). With cooling the substance crystallized. We obtained 4.5 g (80%) of hexafluoroisobutyrophenone, m.p. 35-36.5° (from octane). A mixture with a known sample melted without depression (m.p. 34°).

(α -Iminobenzyl) malononitrile. A mixture of 3.8 g (0.015 mole) of (II) and excess of aqueous ammonia was shaken for six hours. The crystals formed were filtered off and dried. We obtained 2.46 g (98%) of (α -imino-benzyl) malononitrile; m.p. 180-181° (from xylene); λ_{max} : 6.53; 6.33; 5.97; 4.49 μ . Found: C 70.90; H 4.04; N 24.94%. $C_{10}H_7N_3$. Calculated: C 71.00; H 4.17; N 24.83%.

The same compound was obtained by the action of excess of aqueous ammonia on the imine of hexafluoroisobutyrophenone.

Reaction of (II) with Diethylamine. A solution of 13 g (0.05 mole) of (II) in 30 ml of dry ether was added over a period of 20 minutes to a stirred solution of 17 g of diethylamine in 100 ml of ether. The reaction mixture was left overnight and then filtered from the precipitate of $(C_2H_5)_2NH \cdot HF$ (3.9 g; 84% calculated for the replacement of one fluorine atom). The residue was vacuum-distilled. We obtained 14.2 g of slightly colored viscous liquid; b.p. 115-120° (4 mm); n_D^{20} 1.4790; λ_{max} 5.41; 5.97 μ ; melting points of the components of the mixture, determined thermographically: from -63° to -67° and from -90° to -94°. Found: C 53.86; H 4.60; F 37.86%. $C_{14}H_{15}F_6NO$. Calculated: C 54.02; H 4.86; F 36.62%.

A mixture of 7.6 g of the freshly distilled substance and 15 ml of concentrated hydrochloric acid was heated in a water bath. The mixture was cooled and repeatedly extracted with ether. The ether solution was washed with water and dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-distilled. The bulk of the substance came over at 95-100° (5 mm); when cooled, the distillate crystallized. Recrystallization at -30° gave 3.2 g of 3,3,3-trifluoropropiophenone; m.p. 37-37.5° (from octane); λ_{max} : 6.25; 5.85 μ . Found: C 57.41; H 3.77; F 30.31%. $C_9H_7F_3O$. Calculated: C 57.45; H 3.75; F 30.29%.

The 2,4-dinitrophenylhydrazone had m.p. 190-191° (from alcohol). Found: C 48.79; H 2.98%. $C_{15}H_{11}N_4F_3O_4$. Calculated: C 48.92; H 3.01%.

Crystallization of the residue in the flask gave 0.8 g of N,N-diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl) propionamide; m.p. 95.5-96° (from octane); λ_{max} : 6.06 μ . Found: C 54.56; H 5.53; F 31.03; N 4.52%. $C_{14}H_{16}F_3ON$. Calculated: C 54.36; H 5.21; F 30.72; N 4.52%.

Treatment of an ethereal solution of 7.7 g of $C_{14}H_{15}F_6N$ with dilute hydrochloric acid at 0° gave 3.24 g of N,N-diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl) propionamide, m.p. 95°, undepressed by admixture of a previously prepared sample (m.p. 95.5°). N,N-Diethyl-3,3-difluoro-3-phenyl-2-(trifluoromethyl) propionamide is stable to the action of concentrated hydrochloric acid.

1-[1,1,3-Trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine.

The substance (II) (17.3 g; 0.067 mole) was gradually added to piperidine (15 g) in dry ether (50 ml). To avoid a violent reaction the mixture was cooled externally with ice water. After one day the reaction mixture was treated with a mixture of dilute hydrochloric acid and ice. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether extracts were dried over magnesium sulfate. When ether was distilled off, the residue crystallized. We obtained 17.2 g (80%) of 1-[1,1,3-trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine, m.p. 79-81° (from octane). Found: C 55.85; H 4.65; F 35.60; N 4.32. $C_{15}H_{15}F_6N$. Calculated: C 55.73; H 4.68; F 35.25; N 4.32%.

A mixture of 8 g (0.0248 mole) of 1-[1,1,3-trifluoro-3-phenyl-2-(trifluoromethyl) allyl] piperidine and 15 ml of concentrated hydrochloric acid was heated at 60-70° for five hours. There was a vigorous evolution of carbon dioxide. The reaction mixture was diluted with water and extracted with ether, the ether extracts were dried with magnesium sulfate, ether was distilled off, and the residue was vacuum-distilled. We obtained 2.7 g (58%) of 3,3,3-trifluoropropiophenone, m.p. 36.5° (from octane). A mixture with a known sample melted without depression (m.p. 36°).

Reaction of (II) with Ethylamine.

In the course of 30 minutes, 5.75 g (0.1278 mole) of gaseous ethylamine was passed into a solution of 12 g (0.0426 mole) of (II) in 150 ml of dry ether cooled to 0°. There was a voluminous white precipitate of $C_2H_5NH_2 \cdot HF$. The mixture was left overnight. On the next day the precipitate was filtered off, ether was distilled off, and the residue was vacuum-distilled. We obtained 11 g of a fraction boiling over the range 59-84° (10 mm). Hydrolysis of this fraction with concentrated hydrochloric acid gave a semicrystalline mass, the fractional crystallization of which gave 4.2 g (35%) of hexafluoroisobutyrophenone, m.p. 35-36° (from octane). A mixture with a known sample melted without depression (m.p. 35°). Strong cooling of the mother liquor gave an oil, from which we obtained the 2,4-dinitrophenylhydrazone of 3,3,3-trifluoropropiophenone, m.p. 190-191° (from alcohol). A mixture with a known sample melted without depression (m.p. 190°).

Reactions of 1-Alkylheptafluoroisobutenes.

Imine of Butyl Hexafluoroisopropyl Ketone. Dry ammonia was passed for one hour into a solution of 16.7 g (0.07 mole) of (III) in 140 ml of dry ether cooled to 0°. On the next day the precipitate of NH_4F was filtered off. Ether was distilled from the filtrate, and the residue was vacuum-distilled. We obtained 10 g of the imine of butyl hexafluoroisopropyl ketone; b.p. 64° (11 mm); n_D^{20} 1.3840; d_4^{20} 1.2770; found MR 43.05; $\text{C}_8\text{H}_{11}\text{F}_6\text{NF}$. Calculated MR 42.93. Found: C 40.91; H 4.71; F 48.87%. $\text{C}_8\text{H}_{11}\text{NF}_6$. Calculated: C 40.86; H 4.71; F 48.47%.

The benzoyl derivative had m.p. 106-107° (from aqueous alcohol). Found: C 52.59; H 4.44; F 34.30%. $\text{C}_{15}\text{H}_{15}\text{F}_6\text{NO}$. Calculated: C 53.10; H 4.45; F 33.60%.

Butyl Hexafluoroisopropyl Ketone. The imine of butyl hexafluoroisopropyl ketone (4.1 g; 0.0174 mole) was hydrolyzed by treatment with concentrated hydrochloric acid (7 ml) at 80° for three hours. The reaction mixture was extracted with ether, ether was distilled off, and the residue was vacuum-distilled. We obtained 3 g (72%) of butyl hexafluoroisopropyl ketone; b.p. 64-65° (52 mm); n_D^{20} 1.3465; d_4^{20} 1.2569; found MR 40.06; $\text{C}_8\text{H}_{10}\text{F}_6\text{O}$. Calculated MR 39.99; λ_{max} 5.75 μ . Found: C 40.69; H 4.32; F 48.35%. $\text{C}_8\text{H}_{10}\text{F}_6\text{O}$. Calculated: C 40.68; H 4.27; F 48.26%.

Imine of Valerylmalononitrile. The substance (III) (3.85 g; 0.016 mole) was treated with excess of aqueous ammonia. The mixture was shaken for one day. The crystals formed were filtered off. We obtained 1.83 g (75%) of the imine of valerylmalononitrile, m.p. 110-110.5° (from benzene); λ_{max} 6.49; 5.95; 4.44 μ . The substance was dissolved by 50% KOH solution and was reprecipitated on acidification. Found: C 64.58; H 7.48; N 28.35%. $\text{C}_8\text{H}_{11}\text{N}_3$. Calculated: C 64.41; H 7.43; N 28.35%. Analogously, from the corresponding olefins we obtained the imine of propionylmalononitrile in 32% yield; m.p. 164-165° (from xylene); found: C 59.71; H 5.86%. $\text{C}_6\text{H}_7\text{N}_3$. Calculated: C 59.49; H 5.82%; the imine of (4-methylvaleryl)malononitrile in 54% yield; m.p. 100-101° (from xylene); λ_{max} 6.45; 5.95; 4.48 μ . Found: C 66.59; H 8.04; N 25.96%. $\text{C}_7\text{H}_{13}\text{N}_3$. Calculated: C 66.23; H 8.03; N 25.73%.

Reaction of (III) with Diethylamine.

A solution of 22 g (0.32 mole) of diethylamine in 50 ml of dry ether was added with stirring to a solution of 19.3 g (0.08 mole) of (III) in 175 ml of dry ether in an apparatus protected from atmospheric moisture and carbon dioxide. The mixture was left for two days. The ethereal solution was then filtered from the precipitate of diethylamine hydrofluoride (6.97 g; 0.075 mole). Ether was distilled from the filtrate, and the residue was vacuum-fractionated. We obtained 16 g (68%) of N,N-diethyl-1,1,3-trifluoro-2-(trifluoromethyl)-2-heptenylamine, b.p. 100-101° (6.5 mm) and n_D^{20} 1.4293, a viscous liquid which decomposes when kept for a short time. Found: C 49.24; H 6.49%. $\text{C}_{12}\text{H}_{19}\text{F}_6\text{N}$. Calculated: C 49.47; H 6.57%.

The freshly distilled amine (2.6 g; 0.0093 mole) was mixed with dilute hydrochloric acid (10 ml) in a flask fitted with a reflux condenser. Heat was evolved. The mixture was left at room temperature for three days, diluted with 25 ml of water, and extracted with three 15-ml portions of ether. The ether extracts were washed with water and dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-fractionated. We obtained 1.6 g (57%) of N,N-diethyl-3-fluoro-2-(trifluoromethyl)-2-heptenamide; b.p. 110° (4 mm); n_D^{20} 1.4261; d_4^{20} 1.1298; λ_{max} : 5.99; 5.68 μ ; found MR 61.28; $\text{C}_{12}\text{H}_{19}\text{F}_4\text{NO}$. Calculated: MR 61.62. Found: C 53.53; H 7.07; N 5.50%. $\text{C}_{12}\text{H}_{19}\text{F}_4\text{NO}$. Calculated: C 53.52; H 7.11; N 5.19%.

The nuclear magnetic resonance spectrum of F^{19} consisted of two sharply defined resonance peaks with a ratio of amplitudes of 3 : 1, and the higher peak was in the region of absorption of the CF_3 group.

Reaction of (III) with Piperidine.

A solution of 25 g (0.22 mole) of piperidine in 20 ml of ether was added to a solution of 11.6 g (0.0487 mole) of (III) in 40 ml of ether. After a few minutes an exothermic reaction set in, and this was controlled by external cooling. On the next day the precipitate of piperidine hydrofluoride was filtered off (3.15 g; 0.3 mole) and the ether and most of the excess of piperidine were vacuum-distilled off. The viscous residue was treated with excess of dilute (1 : 1) hydrochloric acid. The mixture was left overnight, and the crystals formed were then filtered off. We obtained 10.3 g (75%) of the piperidide of 3-fluoro-2-(trifluoromethyl)-2-heptenoic acid; m.p. 64.5-65° (from aqueous alcohol); λ_{max} : 6.04; 5.80 μ . Found: C 56.32; H 6.92; N 5.06; F 27.38%. $\text{C}_{13}\text{H}_{19}\text{F}_4\text{NO}$. Calculated: C 55.50; H 6.81; N 4.98; F 27.02%.

By an analogous procedure we obtained the following from the corresponding olefins: The piperidide of 3-fluoro-2-(trifluoromethyl)-2-pentenoic acid; m.p. 88-88.5° (from aqueous alcohol); λ_{max} 6.02; 5.80 μ ; yield 64%. Found: C 52.13; H 5.90; F 30.38; N 5.88%. $\text{C}_{11}\text{H}_{15}\text{F}_4\text{NO}$. Calculated: C 52.17; H 5.97; F 30.01; N 5.53%. The piperidide of 3-fluoro-2-(trifluoromethyl)-2-octenoic acid; m.p. 75-76° (from aqueous alcohol); λ_{max} 6.02; 5.80 μ ; yield 69%. Found: C 56.97; H 7.14; F 25.77; N 4.74%. $\text{C}_{14}\text{H}_{21}\text{F}_4\text{NO}$. Calculated: C 56.97; H 7.17; F 25.73; N 4.74%.

Reaction of (III) with Ethylamine.

A solution of 12.1 g (0.051 mole) of (III) in 20 ml of dry ether was added over a period of 30 minutes to a cooled (to 0°) stirred solution of 11.5 g (0.25 mole) of ethylamine in 150 ml of dry ether. The mixture was left for three days. The precipitate of ethylamine hydrofluoride was filtered off, ether was distilled off, and the residue was vacuum-distilled. We obtained 3.5 g (26%) of the ethylimine of butyl hexafluoroisopropyl ketone, which was redistilled, and then had the following constants: b.p. 49-50° (9 mm); n_D^{20} 1.3715; d_4^{20} 1.1626; found: MR 51.40; $C_{10}H_{15}F_6N$. Calculated MR 52.34; Found: C 45.68; H 5.92; F 43.85%. $C_{10}H_{15}F_6N$. Calculated: C 45.62; H 5.74; F 49.31%.

The residue in the distillation flask was a straw-yellow thick mass with a pyridinelike odor. Its hydrolysis with concentrated hydrochloric acid gave 1.2 g of N-ethyl-3-oxo-2-(trifluoromethyl) heptanamide; m.p. 95-97° (from octane) λ_{max} : 5.75; 6.02; 6.41 μ . Found: C 49.90; H 6.69; F 23.86; N 5.89%. $C_{10}H_{16}F_3NO_2$. Calculated: C 50.20; H 6.74; F 23.82; N 5.85%.

Hydrolysis of the Ethylimine of Butyl Hexafluoroisopropyl Ketone.

A mixture of 4 g (0.01519 mole) of the ethylimine of butyl hexafluoroisopropyl ketone and 5 ml of concentrated hydrochloric acid was heated at 60° for 30 minutes. The mixture was then diluted with water and repeatedly extracted with ether. The combined ether extracts were dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-distilled. We obtained 2.4 g (67%) of butyl hexafluoroisopropyl ketone [1,1,1-trifluoro-2-(trifluoromethyl)-3-heptanone], b.p. 62-64° (52 mm) and n_D^{20} 1.3470. The infrared absorption spectrum was identical with that of known butyl hexafluoroisopropyl ketone.

Reaction of Ethyl Perfluoroisobutenyl Ether with Ammonia.

Ethyl 3,3,3-Trifluoro-2-(trifluoromethyl) propionimide. Dry ammonia was passed for one hour into a solution of 24.6 g (0.109 mole) of ethyl perfluoroisobutenyl ether in 200 ml of dry ether cooled to 0°. The mixture was left for one hour, the precipitate of ammonium fluoride was filtered off, ether was distilled off, and the residue was vacuum-distilled. We obtained 13.3 g (55%) of ethyl 3,3,3-trifluoro-2-(trifluoromethyl) propionimide. After redistillation the substance had the following properties: b.p. 48° (111 mm); n_D^{20} 1.3348; d_4^{20} 1.3383; λ_{max} 5.97 μ ; found MR 34.45; $C_6H_7F_6NO$. Calculated MR 35.05. Found: C 32.01; H 2.93; F 51.66%. $C_6H_7F_6NO$. Calculated: C 32.39; H 3.16; F 51.09%.

Hydrolysis of the imidic ester with concentrated hydrochloric acid led to 3,3,3-trifluoro-2-(trifluoromethyl) propionamide, m.p. 155-156° (from aqueous alcohol). A mixture with a known sample melted without depression (m.p. 155-156°). Treatment of the imidic ester with aqueous ammonia gave (ethoxyiminomethyl)malononitrile; m.p. 215-223° (decomp.; from water); λ_{max} : 4.54; 6.02; 6.41 μ . The literature [6] gives m.p. 219-220°. Found: C 52.19; H 5.14; N 30.65%. $C_6H_7N_3O$. Calculated: C 52.55; H 5.03; N 30.64%.

The same compound was obtained by the action of concentrated ammonia on ethyl perfluoroisobutenyl ether; m.p. 217-220° (from water). A mixture with a known sample melted without depression (m.p. 215-217°).

SUMMARY

1. A perfluoroisobutene in which the fluorine atom in the 1-position is replaced by an alkoxy, alkyl, or aryl group reacts with amines and ammonia in the 1- or 3-position; the position attacked is determined both by the structure of the fluoro olefin and the character of the attacking reagent.

2. The reaction of such substituted perfluoroisobutenes with excess of aqueous ammonia leads to the complete elimination of fluorine from the molecule and the formation of derivatives of malononitrile.

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*Original Russian pagination. See C. B. translation.

REACTIONS OF FLUORO OLEFINS

COMMUNICATION 12. REACTIONS OF CHLOROFLUOROBUTENES WITH ALCOHOLS

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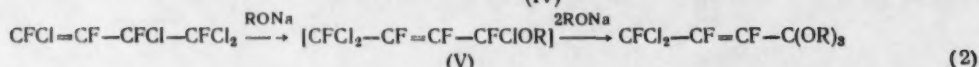
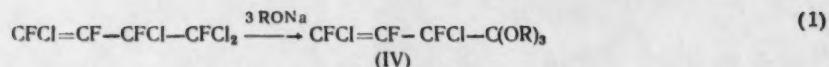
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Questions relating to the conjugation of a carbon-halogen bond with a carbon-carbon double bond in olefins have been extensively investigated, and various relations have been found which show the dependence of reactivity on the structure of the olefin, the character of the reagent, the medium, etc. [1, 2]. However, there is still little information about analogous σ, π -conjugation in polyfluoro olefins. It has been shown that chlorine in perfluoroallyl chloride $\text{CF}_2 = \text{CF}-\text{CF}_2\text{Cl}$ is readily replaced by I, CN, OCH_3 , OC_6H_5 , and $\text{N}(\text{C}_2\text{H}_5)_2$ [3, 5]. The replacement of chlorine by iodine occurs readily in compounds of the type $\text{CF}_2 = \text{CX}-\text{CF}_2\text{Cl}$, but in such halides as $\text{C}_6\text{H}_5\text{CF}_2\text{Cl}$, $\text{CFCl} = \text{CF}-\text{CF}_2\text{Cl}$ and $\text{CCl}_2 = \text{CCl}-\text{CF}_2\text{Cl}$, chlorine is not replaced by iodine, which indicates that the replacement of chlorine in polyfluoroallyl chlorides proceeds by an $\text{S}_\text{N}2'$ mechanism [6, 7]. The occurrence of the same mechanism was proved for the replacement of chlorine by iodine in allyl systems of the type $\text{CF}_2 = \text{CH}-\text{CFCl}_2$ and $\text{CF}_2 = \text{CF}-\text{CFCl}_2$ [8].

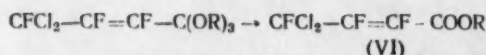
We investigated the action of sodium methoxide and ethoxide on linear dimers of 1,2-dichlorodifluoroethylene and chlorotrifluoroethylene. The first of these dimers has the structure 1,3,4,4-tetrachloro-1,2,3,4-tetrafluoro-1-butene $\text{CFCl} = \text{CF}-\text{CFCICFCI}_2$ (I), which was proved by Haszeldine and Osborne by its oxidation to $\text{CFCI}_2\text{CFCICOOH}$ [9].

No reliable proof of the structure of the linear dimer of chlorotrifluoroethylene has been given in the literature; its oxidation gives only CF_2CICOOH , which is consistent with the structure 1,4-dichlorohexafluoro-2-butene CF_2CICOOH , but Miller [10] considers that it has the structure 3,4-dichlorohexafluoro-1-butene $\text{CF}_2 = \text{CF}-\text{CFCICF}_2\text{Cl}$ (II) because it is readily dehalogenated to $\text{CF}_2 = \text{CF}-\text{CF} = \text{CF}_2$. Moreover, by the dehalogenation of 1,2,3,4-tetrachlorohexafluorobutane with zinc in dioxane, Miller obtained a dichlorohexafluorobutene that did not give perfluorobutadiene under the action of zinc. This compound was assigned the structure (II). This argument is not very convincing, for on dehalogenation $\text{CH}_2 = \text{CH}-\text{CHClCH}_2\text{Cl}$ and $\text{CH}_2\text{Cl}-\text{CH} = \text{CH}-\text{CH}_2\text{Cl}$ give $\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}_2$ with equal readiness [11], and the structure of (II) suggested for the product was not supported by any evidence. There was some hope, however, that a study of reactions with nucleophilic reagents and their comparison with the corresponding reactions of (I) would enable us to resolve the question of the structure of the linear dimer of chlorotrifluoroethylene.

When (I) was treated with sodium methoxide or ethoxide, two chlorine atoms and one fluorine atom were replaced and a trialkoxy compound was obtained which was found to be an ortho ester. It was converted into the ordinary ester by the action of phosphoric oxide or concentrated sulfuric acid. Two schemes of reaction may be proposed:



Comparison of the infrared spectra of (I) and of the substance prepared from it by the action of sodium ethoxide showed that the double bond absorption maxima in these compounds are different: for (I) it is 1700 cm^{-1} , and for the ortho ester it is 1750 cm^{-1} . It is obvious that the double bond absorption maxima for (I) and for a compound of type (IV) will be identical. Hence, it follows from the spectrum data that reaction occurs in accordance with Scheme (2), which leads to 1,1,1-trialkoxy-4,4-dichloro-2,3,4-trifluoro-2-butene (V), the treatment of which with phosphoric oxide or sulfuric acid gives a 4,4-dichlorotrifluorocrotonic ester (VI):



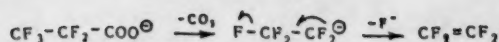
The structures of the ortho and ordinary esters were finally proved by their oxidation with potassium permanganate, when dichlorofluoroacetic acid was isolated. Hence, reaction of (I) with alkoxides is accompanied by allyl rearrangement and probably proceeds by an S_N2' mechanism.

By the action of alkoxides on the linear dimer of chlorotrifluoroethylene, we obtained products in which one chlorine atom was replaced by an alkoxy group. The infrared spectra of these compounds had intense absorption maxima at about 1800 cm^{-1} , which is characteristic of the $\text{CF}=\text{CF}_2$ group [12]. This suggested that the substances were 3-alkoxy-4-chlorohexafluoro-1-butenes $\text{CF}_2=\text{CF}-\text{CF}(\text{OR})-\text{CF}_2\text{Cl}$. In fact, treatment with bromine gave the corresponding dibromides, 3-alkoxy-1,2-dibromo-4-chloro-hexafluorobutanes $\text{CF}_2\text{BrCFBrCF}(\text{OR})\text{CF}_2\text{Cl}$. The hydrolysis of 1,2-dibromo-4-chloro-3-ethoxyhexafluorobutane (VII) with concentrated sulfuric acid gave 3,4-dibromo-1-chloropentafluoro-2-butanone (VIII):

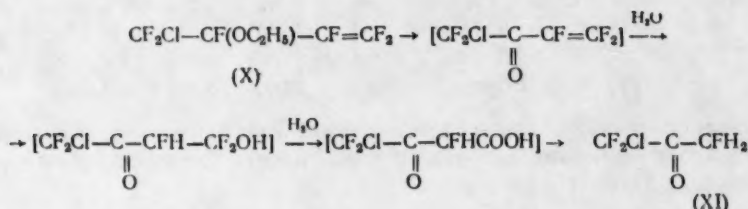


The structure of (VIII) was confirmed by its reactions with ammonia and aniline. These gave the corresponding amides of chlorodifluoroacetic acid, ammonium bromide or aniline hydrobromide, and a gas (probably $\text{CF}_2=\text{CFBr}$).

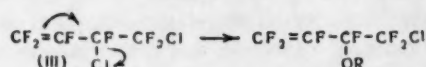
This decomposition is analogous to the cleavage of polyhaloacetones under the action of amines with formation of haloform and an amide [13], but here, because of the presence of bromine atoms in the β -position with respect to the negative charge of the intermediate anion (IX), the stabilization of the latter occurs not by the addition of H^+ , but by the elimination of Br^- . On the other hand, the elimination of β -halogen is similar to the process of decomposition of alkali-metal salts of β -halo acids, which leads to the formation of olefins. Thus, in particular, perfluoro olefins are obtained from perfluoro carboxylic salts [14].



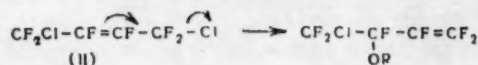
Treatment of 3-ethoxy-4-chlorohexafluoro-1-butene (X) with concentrated sulfuric acid gives 1-chloro-1,1,3-trifluoropropanone (XI):



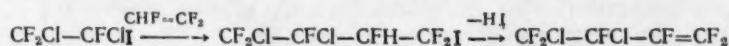
Hence, if it is assumed that the linear dimer of chlorotrifluoroethylene has the structure (III), it follows that in reaction with alkoxides normal replacement of chlorine in the allyl position by an alkoxy group occurs:



It seemed strange that there should be such a great difference between compounds which were so similar in structure, $\text{CFCI}=\text{CF}-\text{CFCI}-\text{CFCI}_2$ and $\text{CF}_2=\text{CF}-\text{CFCI}-\text{CF}_2\text{Cl}$, all the more that anomalous replacement should occur more readily in the second case. It would be much more logical to assume that 3-alkoxy-4-chlorohexafluoro-1-butenes are formed from (II) by an $\text{S}_{\text{N}}2'$ reaction:



We investigated the infrared spectrum of the linear dimer of chlorotrifluoroethylene. It was found that maxima were present at about 1700 and 1780 cm^{-1} (corresponding to the groups $-\text{CF}=\text{CF}-$ and $-\text{CF}=\text{CF}_2$) [12] and the first of these was somewhat more intense. When we take account of the facts that the intensities of lines corresponding to central double bonds are usually lower because of the greater symmetry of the molecule and that (III), synthesized by Tarrant and Lilyquist [15] in accordance with the equation



has only one absorption peak at 1780 cm^{-1} , it may be considered highly probable that the linear dimer of chlorotrifluoroethylene is a mixture of (III) and (II) with a predominance of the latter.

EXPERIMENTAL

4,4-Dichloro-2,3,4-trifluoro-1,1,1-trimethoxy-2-butene. A methanolic solution of sodium methoxide was prepared from 7 g (0.3 g-atom) of sodium and 75 ml of absolute methanol; it was added dropwise with ice cooling and stirring to 26.6 g (0.1 mole) of (I) over a period of 90 minutes. The mixture was left overnight, heated in a water bath at about 70° for 30 minutes, and poured into water. The oil was extracted with ether, and the extract was carefully washed with water and dried with calcium chloride. The residue remaining after removal of ether was vacuum-distilled: yield 20.7 g (77%); b.p. 69.5–72.5° (8 mm). After redistillation: b.p. 56.0° (3.5 mm); n_{D}^{20} 1.4182; d_4^{20} 1.4117; found MR 48.05; calculated for $\text{C}_7\text{H}_2\text{F}_3\text{Cl}_2\text{O}_3$ MR 49.14. Found: C 31.02; H 3.27%. $\text{C}_7\text{H}_2\text{F}_3\text{Cl}_2\text{O}_3$. Calculated: C 31.24; H 3.37%.

4,4-Dichloro-1,1,1-triethoxy-2,3,4-trifluoro-2-butene. This was prepared analogously from 26.6 g of (I), 7.5 g of sodium, and 120 ml of absolute ethanol. Yield 24.5 g (78.6%); b.p. 73-75° (3 mm); after redistillation: b.p. 67.5° (2 mm); n_D^{20} 1.4230; d_4^{20} 1.2607; found MR 62.84; calculated for $C_{10}H_{15}F_3Cl_2O_3$, MR 63.00. Found: F 18.40; Cl 22.91%. $C_{10}H_{15}F_3Cl_2O$. Calculated: F 18.32; Cl 22.79%.

Methyl 4,4-Dichlorotrifluorocrotonate. 4,4-Dichloro-2,3,4-trifluoro-1,1,1-trimethoxy-2-butene (10.5 g) was treated with concentrated sulfuric acid (4 ml). When the vigorous reaction ceased, the mixture was left overnight and then decomposed with water. The oil was extracted with ether, and the ether solution was washed with water and dried with calcium chloride. The residue after removal of ether was vacuum-distilled. We obtained 6.9 g (76%) of methyl 4,4-dichlorotrifluorocrotonate, b.p. 52-55° (8 mm). Redistillation gave a substance having b.p. 49.5-50.5° (7 mm); n_D^{20} 1.4273; d_4^{20} 1.5233; found MR 37.53; calculated for $C_6H_5F_3Cl_2O_2$, MR 36.63. Found: C 27.12; H 1.57; F 25.28%. $C_6H_5F_3Cl_2O$. Calculated: C 26.93; H 1.40; F 25.56%.

4-4-Dichlorotrifluorocrotonamide. This was obtained in 76% yield by treatment of the methyl ester of the acid with aqueous-alcoholic ammonia; m.p. 102-103° (from water). Found: C 23.24; H 1.00; N 6.55%. $C_4H_2F_3Cl_2NO$. Calculated: C 23.09; H 0.97; N 6.73%.

Ethyl 4,4-Dichlorotrifluorocrotonate. Phosphoric oxide (4 g) was added to 4,4-dichloro-1,1-triethoxy-2,3,4-trifluoro-2-butene (6.5 g). When reaction was complete, the product was vacuum-distilled. We obtained 4.2 g (85%) of ethyl 4,4-dichlorotrifluorocrotonate, b.p. 49-51° (3.5 mm). After redistillation: b.p. 47.5° (3 mm); n_D^{20} 1.4299; d_4^{20} 1.4421; found MR 42.35; calculated for $C_6H_5F_3Cl_2O_2$, MR 41.25. Found: C 30.23; H 2.28; F 23.27; Cl 29.42%. $C_6H_5F_3Cl_2O_2$. Calculated: C 30.40; H 2.13; F 24.05; Cl 29.92%.

Oxidation of 4,4-Dichloro-1,1,1-triethoxy-2,3,4-trifluoro-2-butene. 4,4-Dichloro-1,1,1-triethoxy-2,3,4-trifluoro-2-butene (7 g) was added dropwise to a stirred solution of 50 g of potassium permanganate in 100 ml of water at room temperature. When the addition was complete, stirring was continued for a few hours at room temperature and for one hour at 50°. During the whole process, carbon dioxide was passed rapidly through the reaction mixture. The mixture was then treated with sulfur dioxide and filtered; the filtrate was continuously extracted with ether for a few hours. Fractionation of the extract gave 1.2 g of an acid, b.p. 50-55° (11 mm), which was converted in the usual way into the amide, m.p. 127.5-128.5° (from octane). The literature [16] gives m.p. 126.5°. Found: C 16.19; H 1.31; F 13.15; N 9.70%. $C_2H_2FCl_2NO$. Calculated: C 16.45; H 1.38; F 13.02; N 9.60%.

Oxidation of Ethyl 4,4-Dichlorotrifluorocrotonate. The procedure was analogous to that of the preceding experiment. From 13 g of the ester we obtained 3 g of dichlorofluoroacetic acid. The amide had m.p. 127.5-128.5°, undepressed by admixture of the sample obtained in the preceding experiment.

4-Chlorohexafluoro-3-methoxy-1-butene. A methanolic solution of sodium methoxide prepared from 1.85 (0.08 g-atom) of sodium and 25 ml of absolute methanol was added dropwise over a period of 6.5 hours with ice cooling and stirring to 37 g (0.16 mole) of the linear dimer of chlorotrifluoroethylene. When the addition was complete, stirring was continued further for 90 minutes at room temperature, and the reaction mixture was then decomposed with water; the oil was separated, washed with water, and dried with calcium chloride. Fractionation gave 19.0 g of unchanged olefin and 9.4 g (51.4%) of 4-chlorohexafluoro-3-methoxy-1-butene, b.p. 90-95° (739 mm). After redistillation: b.p. 47-48° (148 mm); n_D^{20} 1.3434; d_4^{20} 1.5114; found MR 32.01; calculated for $C_6H_5F_6ClO$, MR 32.17. Found: C 26.78; H 1.37; F 48.90%. $C_6H_5F_6ClO$. Calculated: C 26.27; H 1.32; F 49.88%.

4-Chloro-3-ethoxyhexafluoro-1-butene. This was prepared analogously from 29 g (0.125 mole) of dimer, 1.73 g (0.075 g-atom) of sodium, and 30 ml 100% C_2H_5OH . We obtained 9.0 g of unchanged olefin and 9.8 g (54%) of 4-chloro-3-ethoxyhexafluoro-1-butene, b.p. 63-67° (149 mm). After redistillation: b.p. 60-61° (149 mm); n_D^{20} 1.3462; d_4^{20} 1.4252; found MR 36.26; calculated for $C_6H_5F_6ClO$, MR 36.79. Found: C 29.66; H 2.04; F 47.18; Cl 14.63%. $C_6H_5F_6ClO$. Calculated: C 29.71; H 2.08; F 47.00; Cl 14.62%.

1,2-Dibromo-4-chlorohexafluoro-3-methoxybutane. Excess of dry bromine was added to 7.5 g of 4-chlorohexafluoro-3-methoxy-t-butene at room temperature. The mixture was left for one day and then treated with sodium bisulfite solution, washed with water, dried with calcium chloride, and vacuum-distilled. The yield of 1,2-dibromo-4-chlorohexafluoro-3-methoxybutane, b.p. 70-73° (18 mm), was 9.5 g (74.5%). After redistillation: b.p. 73-74° (19 mm); n_D^{20} 1.4240; d_4^{20} 2.0983; found MR 47.23; calculated for $C_5H_3F_6Br_2ClO$, MR 48.17. Found: C 14.90; H 0.72%. $C_5H_3F_6Br_2ClO$. Calculated: C 15.46; H 0.78%.

1,2-Dibromo-4-chloro-3-ethoxyhexafluorobutane. This was prepared analogously from 12.4 g of 4-chloro-3-ethoxyhexafluoro-1-butene. Yield 14.5 g (70.4%); b.p. 74-76° (15 mm); n_D^{20} 1.4195; d_4^{20} 1.9656; found MR 51.76; calculated for $C_6H_5F_6Br_2ClO$ MR 52.79. Found: C 17.67; H 1.20; F 27.73%. $C_6H_5F_6Br_2ClO$. Calculated: C 17.91; H 1.25; F 28.33%.

3,4-Dibromo-1-chloropentafluoro-2-butanone. A mixture of 15 g of 1,2-dibromo-4-chloro-3-ethoxyhexafluorobutane and 5 ml of concentrated sulfuric acid was stirred at 110-115° for six hours. When cool, the reaction mixture was extracted with dry methylene chloride; the residue remaining after the removal of methylene chloride was vacuum-distilled. We obtained 8.0 g (56.7%) of 3,4-dibromo-1-chloropentafluoro-2-butanone, b.p. 55-57° (43 mm). After redistillation: b.p. 56.5-57° (45 mm); n_D^{20} 1.4150; d_4^{20} 2.1120; found MR 42.01; calculated for $C_4F_5Br_2ClO$ MR 41.78. Found: C 13.82; F 26.30%. $C_4F_5Br_2ClO$. Calculated: C 13.56; F 26.81%.

Chlorodifluoroacetamide. Dry ammonia was passed into a solution of a little 3,4-dibromo-1-chloropentafluoro-2-butanone in dry ether. Ammonium bromide was filtered off, ether was evaporated, and the residue was crystallized from octane. This gave the amide of chlorodifluoroacetic acid, m.p. 80-81° undepressed by admixture of a known sample (m.p. 80-81°). The literature [17] gives m.p. 78.5°.

2-Chloro-2,2-difluoroacetanilide. An ethereal solution of a little of the ketone was treated with excess of aniline. When the reaction was finished (the reaction was accompanied by the liberation of gas, probably $CF_2 = CFBr$), the precipitate of aniline hydrobromide was filtered off and the filtrate was washed with dilute hydrochloric acid. The residue remaining after the removal of ether was crystallized from octane; m.p. 72-73°. Found: C 47.02; H 3.06; F 18.39; N 6.94%. $C_9H_6F_2ClNO$. Calculated: C 46.73; H 2.94; F 18.48; N 6.81%.

1-Chloro-1,1,3-trifluoro-2-propanone. A mixture of 17.0 g of 4-chloro-3-ethoxyhexafluoro-1-butene and 5 ml of concentrated sulfuric acid was stirred at room temperature. A vigorous exothermic reaction soon began; it was accompanied by a copious evolution of hydrogen fluoride. After one day distillation of the reaction mixture gave 8 g of 1-chloro-1,1,3-trifluoropropanone (temperature in the vapor during distillation, 70-80°). Redistillation gave a substance having: b.p. 41.5-43° (165 mm); n_D^{20} 1.3510; d_4^{20} 1.4988; found MR 21.09; calculated for $C_3H_2F_3ClO$ MR 21.35. Found: C 24.16; H 1.23; F 38.08%. $C_3H_2F_3ClO$. Calculated: C 24.59; H 1.38; F 38.90%. The 2,4-dinitrophenylhydrazone had m.p. 128-129.5° (from methanol). Found: N 17.35%. $C_9H_6F_3ClN_4O_4$. Calculated: N 17.15%.

SUMMARY

1. The action of sodium alkoxides on 1,3,4,4-tetrachloro-1,2,3,4-tetrafluoro-1-butene leads to the formation of 1,1,1-trialkoxy-4,4-dichloro-2,3,4-trifluoro-2-butenes.

2. When sodium alkoxides react with the linear dimer of chlorotrifluoroethylene, 3-alkoxy-4-chlorohexafluoro-1-butenes are formed. The linear dimer of chlorotrifluoroethylene is probably a mixture of 3,4-dichlorohexafluoro-1-butene and 1,4-dichlorohexafluoro-2-butene, with a predominance of the latter.

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CONDENSATION OF DICHLORODIMETHYLSILANE IN SILENT DISCHARGES

D. N. Andreev

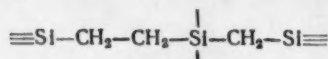
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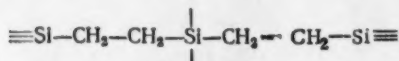
February, 1960

Original article submitted July 4, 1958

It was reported in previous communications [1, 2] that under the action of silent discharges trichloromethylsilane forms a mixture of linear polymers in which silicon and carbon atoms alternate in the main chain, in particular, 1,1,1,3,3-pentachloro-1,3-disilabutane, 1,1,1,4,4-pentachloro-1,4-disilapentane, and isomeric compounds of composition $C_3H_7Cl_3Si_3$ and $C_4H_9Cl_3Si_3$, containing the following groupings in the main chains:

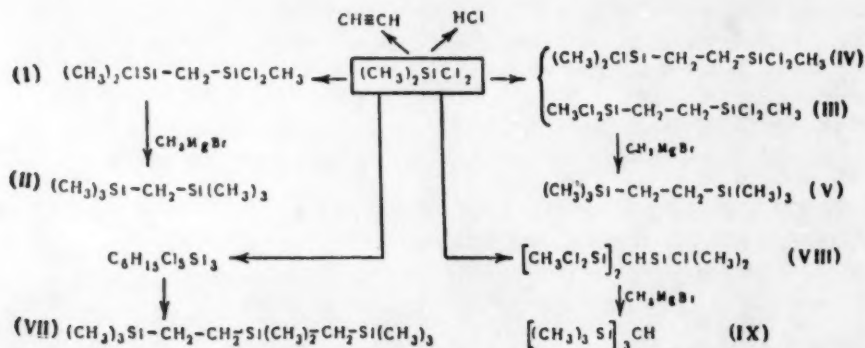


and



In continuation of our investigations on the condensation of various organosilicon compounds in silent discharges, we have carried out the condensation of dichlorodimethylsilane and investigated the compositions of the compounds formed. The results are reported in the present communication.

Experiments on the condensation of $(CH_3)_2SiCl_2$ were carried out in the previously described apparatus and under the conditions used previously [2]. We started with 1290 g of dichlorodimethylsilane and obtained 1050 g of condensate, the fractionation of which yielded 305 g of condensation products of b.p. above 100° (about 70% yield on the dichlorodimethylsilane that reacted and 29-30% yield on the dichlorodimethylsilane originally taken). To determine the compositions and structures of the products, the condensate was fractionated and the isolated compounds were investigated. To confirm the structures of the chloro sila-hydrocarbons obtained, they were converted into unsubstituted sila-hydrocarbons by the action of CH_3MgBr .

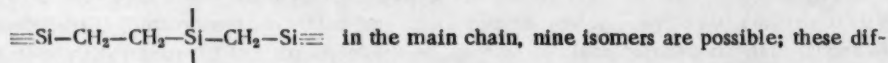


As will be seen from the scheme, the main condensation products obtained from dichlorodimethylsilane were formed by the condensation of two or three $(\text{CH}_3)_2\text{SiCl}_2$ molecules, and also of HCl . Also, the formation of small amounts of acetylene was noted. All the polymers obtained were of linear structure, had a main chain of alternating silicon and carbon atoms, and were therefore compounds of the same type as those obtained previously by the condensation of CH_3SiCl_3 . The isolated 2,2,4-trichloro-4-methyl-2,4-disilapentane (I) had constants close to those of the compound described previously by Clark [3], and under the action of CH_3MgBr it gave 2,2,4,4-tetramethyl-2,4-disilapentane (II).

By the methylation of the fractions of b.p. 87-88° and 88-91° (9 mm), we obtained 2,2,5,5-tetramethyl-2,5-disilaheptane (V), which indicates that these fractions contained compounds in which the hydrocarbon bridge $-\text{CH}_2-\text{CH}_2-$ occurred between silicon atoms in the main chain. Comparison of the constants of these fractions with data in the literature showed that the fractions probably contained a mixture of 2,2,5,5-tetrachloro-2,5-disilaheptane (III) and 2,2,5-trichloro-5-methyl-2,5-disilaheptane (IV). The densities and refractive indices of the fractions isolated were lower than those of pure (III), described by Shostakowski and Kochkin [4] but higher than those of compounds of the composition $\text{C}_5\text{H}_{13}\text{Cl}_3\text{Si}_2$, e.g., 1,1,1-trichloro-4,4-dimethyl-1,4-disilapentane [5]. The analytical data also indicated a mixture of (III) and (IV).

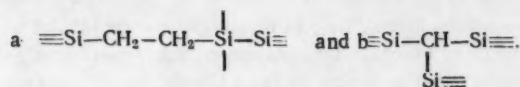
The formation of (III) can be readily explained by the recombination of two $\text{CH}_3\text{Cl}_2\text{SiCH}_2$. As regards (IV) this compound was probably formed by the methylation of (III) by free CH_3 radicals. The possibility of the occurrence of alkylation and arylation reactions of this sort under the action of silent discharges was shown by us earlier in the case of the formation of 1,1,1,4,4-pentachloro-1,4-disilapentane from CH_3SiCl_3 [1, 2] and trichloro (phenyl)- or trichloro (cyclohexyl)-silanes from SiCl_4 and benzene or cyclohexane [6].

In the methylation of chloro sila-hydrocarbons containing three silicon atoms we obtained two sila-hydrocarbons: 2,2,5,5,7,7-hexamethyl-2,5,7-trisilaheptane (VII) and tris(trimethylsilyl)methane (IX). For chloro sila-hydrocarbons of composition $\text{C}_6\text{H}_{15}\text{Cl}_5\text{Si}_3$ (VI), containing the grouping



fer in the distribution of five chlorine atoms and three methyl groups in the side chains. It is most probable that (VI) was a mixture of two isomers, 2,2,5,7,7-pentachloro-5-methyl-2,5,7-trisilaheptane and 2,2,5,5,7-pentachloro-7-methyl-2,5,7-trisilaheptane, which can be readily formed by chain processes from (III) and (IV). The presence of other isomers containing the groupings $(\text{CH}_3)_3\text{Si}-$, $\text{Cl}_3\text{Si}-$, $-\text{CH}_2-\text{Si}(\text{CH}_3)_2\text{CH}_2-$ and others is less probable because their formation requires the occurrence of various secondary reactions, e.g. isomerization.

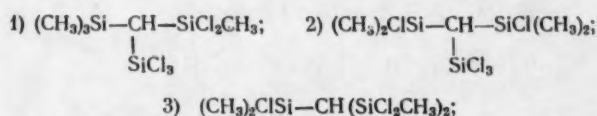
Chloro sila-hydrocarbons of composition $\text{C}_5\text{H}_{13}\text{Cl}_5\text{Si}_3$ (VIII) may have main chains with the following two structures:



The presence of compounds containing the grouping $\equiv\text{Si}-\text{CH}_2-\overset{\textstyle |}{\text{Si}}-\text{CH}_2-\text{Si}\equiv$ in their main chains is excluded because the sila-hydrocarbon (IX) obtained by the methylation of (VIII) differs considerably in its constants from 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane, which has been described in the literature [7].

Comparison of the molecular refractions given in the table leads to the conclusion that compounds (VIII) and (IX) must have the structure (b).

Three isomers are possible for chloro sila-hydrocarbons having this structure:



The presence of the first two isomers is not very probable, because they both contain the SiCl_3 (and the first contains also the $\text{Si}(\text{CH}_3)_3$ group), which is absent in the original dichlorodimethylsilane molecule. The occurrence of various complex secondary reactions must be assumed for their formation. It is most probable that (VIII) has the last structure, which is that of (chlorodimethylsilyl)bis(dichloromethylsilyl)methane. On methylation it will give tristrimethylsilylmethane (IX).

In a recently published paper by Muller and Seitz [8] a compound was described which these authors consider to have the structure tristrimethylsilylmethane. However, the constants of this compound are greatly different from those which we obtained for (IX). This compound was obtained by Muller and Seitz by the action of CH_3MgBr on trichlorosilylmethane. This last compound was isolated from a condensate obtained by passing chloroform over a mixture of metallic silicon and copper at 300° . From the values of density and refractive index given in Muller and Seitz's paper, we have calculated the molecular refraction of the compound that they obtained. Below, for comparison purposes, we give the molecular refraction calculated for tristrimethylsilylmethane from Warrick's data [9] and values calculated from Muller and Seitz's and our experimental results:

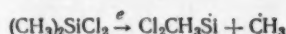
	Chloro sila-hydro- carbons $\text{C}_3\text{H}_9\text{Cl}_3\text{Si}$ MR_D	Sila-hydro- carbons $\text{C}_{10}\text{H}_{21}\text{Si}_4$ MR_D
Calculated for compounds having:		
Structure (a)	77,37	79,46
" (b)	75,47	77,32
Found for (VIII)	75,54	—
" (IX)	—	77,95

Calculated for tristrimethylsilylmethane	$MR_D = 77,32$
Found from Muller and Seitz's data	$MR_D = 76,63$
Found from our data	$MR_D = 77,95$

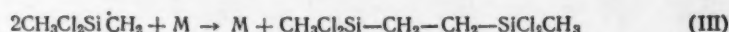
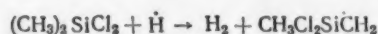
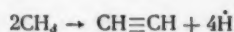
Comparison of these values shows that the molecular refractions of the compounds obtained by Muller and Seitz and by us differ from the theoretically calculated value by equal amounts ($\pm 0,63$ - $0,69$) so that it is not possible by this means to decide which of the two compounds really has the structure of tristrimethylsilylmethane. It would appear that this question could be resolved by the preparation of tristrimethylsilylmethane by some synthetic method which insured the preparation of a compound of this structure.

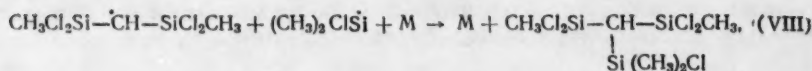
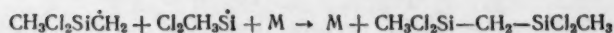
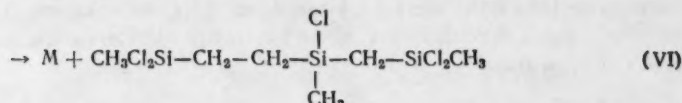
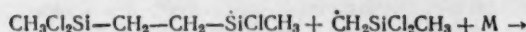
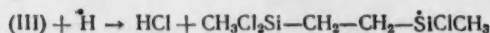
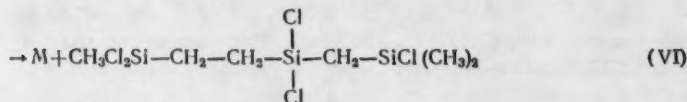
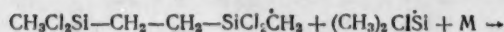
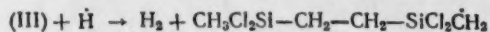
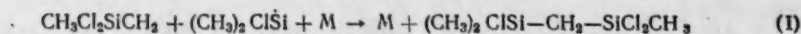
The chloro sila-hydrocarbons which we identified were undoubtedly formed by chain processes proceeding with the participation of hydrogen atoms and various free radicals. The close resemblance in type and structure between the compounds obtained in the present experiments and in those on the condensation of CH_3SiCl_3 [1, 2] gives us reason to suppose that the mechanism by which they are formed is the same in the two cases. The structures of the compounds isolated indicate that the main condensation reactions undergone by chloromethylsilanes under the action of silent discharges are 1) reactions in which new C-C bonds are formed, and 2) reactions in which new Si-C bonds are formed. The predominance in condensates obtained from CH_3SiCl_3 and $(\text{CH}_3)_2\text{SiCl}_2$ of compounds containing two and three silicon atoms, i.e., of relatively low molecular weight, indicates that the chain condensation process is accompanied by chain termination probably due mainly to the recombination of radicals in the bulk phase. These recombination processes were favored by our experimental conditions: atmospheric pressure in the reactor and a short distance between the walls of the reactor.

The primary process will be the cleavage of the Si-CH_3 in $(\text{CH}_3)_2\text{SiCl}_2$ with formation of the free radicals $\text{Cl}_2\text{CH}_2\text{Si}$ and CH_3 , which are initiators for chain reactions:



The formation of the compounds that we identified can be explained by the occurrence of the following chain reactions:





in which M is a third particle that can accept excess of energy.

EXPERIMENTAL

The condensation of dichlorodimethylsilane in silent discharges was carried out under conditions analogous to those for the experiments with trichloromethylsilane [2, 3]. The discharge tube had the following principal dimensions: internal diameter of external electrode 22 mm, external diameter of internal electrode 12 mm, length of discharge zone 300 mm, volume of reaction (discharge) space 80 ml. The high-tension current of frequency 50 cycles/second was obtained from a single-phase 60-kv oil transformer. The experiments were carried out at 24.5 kv and 2.25 ma. The power of the discharge was 55 w, and the mean specific power was 0.68 w/cc (the measurements were made in a secondary circuit).

To accumulate condensation products, six experiments were carried out under standard conditions: a charge of 215 g of dichlorodimethylsilane and a reaction time of 60 hours. As a result of these experiments 1290 g of dichlorodimethylsilane gave 1050 g of a yellow condensate, which was fractionated through a column of 10-12 theoretical plates. We isolated 305 g of condensation products of b.p. above 100°; these were refractionated, first at atmospheric pressure and then under reduced pressure for the higher-boiling products. All the fractions isolated were clear colorless liquids which decomposed rapidly under the action of atmospheric moisture.

Investigation of Individual Fractions of the Condensate

Fraction VIII: b.p. 184-186°; n_D^{20} 1.4602; d_4^{20} 1.1421. Found: Si 25.30; Cl 46.73%. MR 53.18. $\text{C}_4\text{H}_{11}\text{Cl}_3\text{Si}_2$. Calculated: Si 25.33; Cl 47.98%. MR 52.69. For 2,2,4-trichloro-4-methyl-2,4-disilapentane the literature [3] gives m.p. 186° and d_{25}^{20} 1.160.

Hence, Fraction VIII, and also VII, which has similar constants (b.p. 180-184°, n_D^{20} 1.4583; d_4^{20} 1.1309), is 2,2,4-trichloro-4-methyl-2,4-disilapentane (I). Yield 10%.

Fraction I': b.p. 86-87° (9 mm); n_D^{20} 1.4658; d_4^{20} 1.2142. Found: Si 22.47; Cl 48.9%. $\text{C}_4\text{H}_{10}\text{Cl}_4\text{Si}_2$. Calculated: Si 21.92; Cl 55.38%. $\text{C}_5\text{H}_{13}\text{Cl}_3\text{Si}_2$. Calculated: Si 23.83; Cl 45.13%. This fraction, and also the neighboring fractions II' and III' (b.p. 87-88° and 88-91°; n_D^{20} 1.4660; d_4^{20} 1.2145-1.2178) contains a mixture of 2,2,5-trichloro-5-methyl-2,5-disilahexane (IV) and 2,2,5,5-tetrachloro-2,5-disilahexane (III). Yield 14%.

Fraction V': b.p. 115-125° (9 mm); n_D^{20} 1.4832; d_4^{20} 1.2463. Found: Si 24.43; Cl 49.96%; MR 79.92. $C_6H_{15}Cl_5Si_3$. Calculated: Si 24.18; Cl 50.84%; MR 80.10.

This fraction is probably a mixture of two isomers of composition $C_6H_{15}Cl_5Si_3$ (VI); namely 2,2,5,7,7-pentachloro-5-methyl-2,5,7-trisilaoctane and 2,2,5,5,7-pentachloro-7-methyl-2,5,7-trisilaoctane. Yield 5.6%.

Fraction VII': b.p. 135-145° (9 mm); n_D^{20} 1.4897; d_4^{20} 1.2803. Found: Si 24.81, Cl 53.35%. MR 75.54. $C_6H_{13}Cl_5Si_3$. Calculated: Si 25.17; Cl 52.97%, MR 75.47. This fraction contains (chlorodimethylsilyl)bis(dichloromethylsilyl) methane (VIII). Yield 3.0%.

Investigation of Fractions VII-X, B.P. 180-199°

A Grignard reagent was prepared from 24.3 g (1 g-atom) of magnesium and methyl bromide in 400 ml of dry ether, and an ethereal solution of 32 g of the combined Fractions VII-X was added. We obtained 20.4 g of methylation products, the fractionation of which gave 12 g of a substance of b.p. 132-134°; n_D^{20} 1.4180; d_4^{20} 0.7522. found: MR 53.80; calculated: MR 53.73. For 2,2,4,4-tetramethyl-2,4-disilapentane the literature gives: b.p. 134°; n_D^{20} 1.4172; d_4^{20} 0.7520 (7); o.p. 134°; n_D^{20} 1.4178, and d_4^{20} 0.7516 [10]. Hence, the substance isolated (II) is 2,2,4,4-tetramethyl-2,4-disilapentane.

Investigation of Fractions I'-IV', B. P. 86-115° (9 mm)

A Grignard reagent was prepared from 24.3 g (1 g-atom) of magnesium and methyl bromide in 400 ml of dry ether, and an ethereal solution of 42.2 g of the combined Fractions I'-IV' was added. We obtained 24.5 g of methylation products, the fractionation of which gave 10.3 g of a substance of b.p. 151-153°; n_D^{20} 1.4200; d_4^{20} 0.7538; found MR 58.56; calculated MR 58.36. For 2,2,5,5-tetramethyl-2,5-disilaheptane the literature gives: b.p. 150-151°; n_D^{20} 1.4204; d_4^{20} 0.7536 [11]; b.p. 150°; n_D^{20} 1.4200, and d_4^{20} 0.7566 [12]. Hence, the substance isolated (V) is 2,2,5,5-tetramethyl-2,5-disilaheptane.

Investigation of Fractions V'-IX', B.P. 115-180° (9 mm)

A Grignard reagent was prepared from 36.5 g (1.5 g-atoms) of magnesium and methyl bromide in 500 ml of dry ether, and an ethereal solution of 40 g of the combined Fractions V'-IX' was added. We obtained 25.7 g of methylation products, refractionation of which gave two sila-hydrocarbons 1) and 2) in amounts of 5.0 g and 4.1 g, respectively.

1) B.p. 195-196°; n_D^{20} 1.4418; d_4^{20} 0.7892; found MR 77.95; calculated MR 77.32. Found: Si 36.11; 36.38; C 51.49; 51.28; H 12.19; 12.36%. $C_{10}H_{28}Si_3$. Calculated: Si 36.22; C 51.64; H 12.18%.

2) B.p. 214-218°; n_D^{20} 1.4482; d_4^{20} 0.8048; found MR 82.06; calculated MR 81.95. Found: Si 33.79; 33.74; C 53.79; 53.86; H 12.39; 12.19%. $C_{11}H_{30}Si_3$. Calculated: Si 34.26; C 53.57; H 12.26%.

The compound 1) has the composition $C_{10}H_{28}Si_3$; however, its boiling point and other constants differ from those of 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane (b.p. 206°; n_D^{20} 1.4420; d_4^{20} 0.7987), as described in the literature [7]. It is probable that this compound is an isomer of the above compound and is tris(trimethylsilyl)methane (IX). In composition and constants compound (2) corresponds to 2,2,5,5,7,7-hexamethyl-2,5,7-trisilaoctane (VII) [b.p. 87-92° (10 mm); n_D^{20} 1.4470; d_4^{20} 0.8051], which has been described previously [2].

SUMMARY

1. Dichlorodimethylsilane has been condensed under the action of silent discharges, and the composition of the condensate has been investigated. The main reaction products were chloro sila-hydrocarbons in which silicon and carbon atoms alternate in the main chain, which were formed by the condensation of two or three $(CH_3)_2SiCl_2$ molecules. The yield of condensation products was 68-70% on the amount of dichlorodimethylsilane that reacted.

2. The formation of the following compounds was proved: 2,2,4-trichloro-4-methyl-2,4-disilapentane, 2,2,5-trichloro-5-methyl-2,5-disilaheptane, 2,2,5,5-tetrachloro-2,5-disilaheptane, isomers of composition $C_6H_{15}Cl_5Si_3$ (probably 2,2,5,7,7-pentachloro-5-methyl-2,5,7-trisilaoctane and 2,2,5,5,7-pentachloro-7-methyl-2,5,7-trisilaoctane), and (chlorodimethylsilyl)bis(dichloromethylsilyl)methane.

3. The experiments proved that the main chemical processes occurring under the action of silent discharges are the creation of new Si-C and C-C bonds as the result of chain processes.

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*Original Russian pagination. See C. B. translation.

ORIENTATION IN THE CHLORINATION AND BROMINATION OF PHENYLSILANES CONTAINING SiF_3 AND $\text{Si}(\text{CH}_3)_3$ GROUPS

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The orienting effect of silyl groups in the benzene nucleus was first described in 1935 by Kipping and Cusa [1], who established that in the nitration of ethylphenylsilanes the ortho-para-orienting effect of the X_nSi group ($\text{X} = \text{C}_6\text{H}_5, \text{C}_2\text{H}_5$) changes regularly into a meta-orienting effect as the less electronegative ethyl groups are replaced by the more electronegative phenyl groups, i.e., as we pass from $(\text{C}_2\text{H}_5)_3\text{Si}$ to $(\text{C}_6\text{H}_5)_3\text{Si}$ [Curve 3, Fig. 1; n is the number of electronegative Cl or F atoms or phenyl groups in the orienting group $\text{R}_{3-n}(\text{X})_n\text{Si}$]. As we have shown [2,3], in the chlorination of ethylfluorosilanes and chloroethylsilanes, a similar replacement of ethyl groups by fluorine or chlorine leads to an intensification of the β -directing effect of fluoro- and chloro-silyl groups (Fig. 1, Curves 2 and 5).

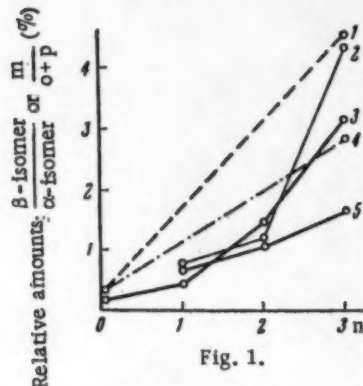
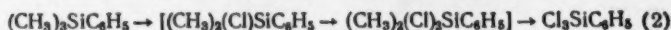
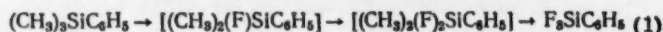


Fig. 1.

To make an approximate evaluation of the extent to which the orienting effect of the same group changes in the case of the chlorination of alkylfluoro (or chloro) phenylsilanes, we considered the extreme members of these two series,



namely $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$, $\text{F}_3\text{SiC}_6\text{H}_5$, and $\text{Cl}_3\text{SiC}_6\text{H}_5$. As the relative amounts of isomers in the chlorination of $\text{Cl}_3\text{SiC}_6\text{H}_5$ in presence of iron powder were determined by us previously ($\text{o} : \text{m} : \text{p} = 24 : 74 : 2$, [4,5]), in the present work we studied the chlorination of only $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ and $\text{F}_3\text{SiC}_6\text{H}_5$. The chlorination of

these compounds under the same conditions gave the following results:

	$\text{F}_3\text{SiC}_6\text{H}_5$	$(\text{CH}_3)_3\text{SiC}_6\text{H}_5$
Ortho (%)	18 (18)	51
Meta (%)	82 (79)	24
Para (%)	— (<3)	25

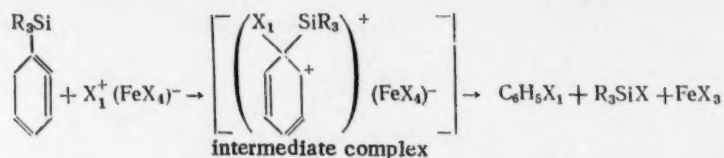
As Fig. 1 shows, these results are fully in accord with those which we obtained in the chlorination of chloroethylsilanes and ethylfluorosilanes: the stronger the β -directing effect of the given X_nSi group (Curves 2 and 5), the greater will be its meta-orienting effect in the chlorination of alkylhalophenylsilanes (Curves 1 and 4). In this respect the F_3Si and Cl_3Si groups are quite analogous to the CF_3 group [2].

Study of the chlorination of alkylhalophenylsilanes reveals some other peculiar features of the reaction: 1) As would be expected, $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ behaves differently in ionic and in free-radical chlorination. In ionic chlorination in presence of iron powder, substitution of chlorine occurs only at C-H bonds in the nucleus with considerable cleavage of the original $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ at an Si-C bond by means of chlorine or HCl^* . On the other hand, photochemical chlorination, which is clearly of a free-radical character, and chlorination with SO_2Cl_2 lead to substitution only at the C-H bonds of the methyl groups with very slight chlorination of the nucleus. Here there is practically no cleavage of the Si-C bond. 2) Cleavage of an Si-C bond in the original halophenylsilane in chlorination in presence of iron powder is observed not only with $(\text{CH}_3)_2(\text{Cl})\text{SiC}_6\text{H}_5$ and $(\text{CH}_3)(\text{Cl})_2\text{SiC}_6\text{H}_5$, but also to some extent with $\text{F}_3\text{SiC}_6\text{H}_5$. 3) The chlorination of $\text{Cl}_3\text{SiC}_6\text{H}_5$ under these conditions is not accompanied by side reactions in which cleavage at an Si-C bond occurs. 4) It is probable that, as a result of the difference in the rates of chlorination of the o-chlorophenyl-, m-chlorophenyl-, and p-chlorophenyl trichlorosilanes formed in the first stages of chlorination, the relative amounts of these vary from experiment to experiment, depending on the amount of dichloro compounds formed. In some experiments, in which the amount of dichloro compounds was considerable, trichloro(o-chlorophenyl)silane was present in the mixture only in very small amounts. 5) Investigation of the

composition of the dichloro compounds showed that, even in the simple case of $\text{Cl}_3\text{Si}-\text{C}_6\text{H}_4-\text{Cl}$ both possible isomers are formed. It will be clear that the composition of the dichloro compounds formed directly from $\text{Cl}_3\text{SiC}_6\text{H}_5$ will be still more complex, for six different isomeric dichloro compounds can be formed from o-chlorophenyl-, m-chlorophenyl-, and p-chlorophenyl silanes.

Of these peculiar features the most noteworthy is the difference in the ease with which the SiCl_3 and SiF_3 groups, and also the $\text{Si}(\text{CH}_3)_3$, $\text{Si}(\text{CH}_3)_2\text{Cl}$, and $\text{Si}(\text{CH}_3)\text{Cl}_2$ groups, are split from the benzene nucleus. In this respect, the most unusual was the elimination of the SiF_3 group in chlorination in presence of iron powder. In bromination under these conditions, the elimination of these groups did not proceed so readily as in chlorination. As in chlorination, the most rapidly eliminated group was $(\text{CH}_3)_3\text{Si}$, and then followed the F_3Si group in $\text{F}_3\text{SiC}_6\text{H}_5$ and $\text{F}_3\text{SiC}_6\text{H}_4\text{Cl}$. The F_3Si group in $\text{F}_3\text{SiCH}_2\text{C}_6\text{H}_5$ was not eliminated at all: Bromination of the nucleus in the para position occurred. On the basis of the experimental data all the compounds studied can be placed in the following order of increasing resistance to the elimination of silyl groups in these reactions: $(\text{CH}_3)_3\text{SiC}_6\text{H}_5 < \text{F}_3\text{SiC}_6\text{H}_5 < \text{F}_3\text{SiC}_6\text{H}_4\text{Cl-m} < \text{F}_3\text{SiCH}_2\text{C}_6\text{H}_5$, $\text{Cl}_3\text{SiC}_6\text{H}_5$. In this respect $(\text{CH}_3)_2(\text{Cl})\text{SiC}_6\text{H}_5$ and $(\text{CH}_3)(\text{Cl})_2\text{SiC}_6\text{H}_5$, as also $\text{F}_3\text{SiC}_6\text{H}_5$, occupy an intermediate position between the extreme members of the series.

As we pass from the $\text{Si}(\text{CH}_3)_3$ group to the SiCl_3 group the tendency for cleavage to occur falls sharply in a manner which is analogous to the increase of stability to β -decomposition in compounds of type $\text{X}_3\text{SiCH}_2\text{CH}_2\text{Cl}$ as alkyl groups X are replaced by chlorine atoms. It may be supposed that, in accordance with the usual mechanism of electrophilic substitution, electrophilic attack of the aromatic nucleus by Cl^+ , Br^+ , and H^+ cations, which leads to the formation of an intermediate complex, is accompanied by nucleophilic attack of silyl groups by Cl^- and Br^- anions. This process evidently occurs as a result of the reactions of $\text{X}^+ [\text{FeX}_4]^-$ complexes with the aromatic nucleus and the silyl groups that are directly attached to it. With the removal of the silyl group from the nucleus, the action of these factors is modified:

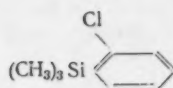


in which R may be alkyl, chlorine, or fluorine, X_1 is chlorine, bromine, or hydrogen, and X is halogen.

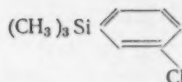
*I.e., HCl liberated in the reaction. When the high stability of (chlorophenyl)trimethylsilanes to HCl is considered [6] (particularly that of the meta-isomer), the occurrence of this cleavage cannot in our case [presence of a large excess of $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$, which very readily undergoes cleavage] have a substantial effect on the values of the relative amounts of isomers found above. This is confirmed by the fact that in the nitration of $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$, in which the same reaction occurs to some extent, the $(\text{CH}_3)_3\text{Si}$ group is again ortho-para orienting [7, 8].

The tendency for the group SiR_3 to be split off, as also in the case of β -decomposition, is determined by the induction and steric effects of R, the electrophilic character of the silicon, and other factors. On the basis of such a hypothesis, we may explain why the F_3Si group is eliminated more readily than the Cl_3Si group. The explanation is evidently that the electronegative fluorine atoms, though much more electrophilic than silicon, cannot substantially counteract nucleophilic attack on the silicon atom, which is of enhanced electrophilic character because of the operation of steric and other factors. It is possible that the increase in the yield of ortho isomers is associated with this. Finally, the same hypothesis provides an explanation for the higher tendency of $\text{C}_2\text{H}_5\text{Si}(\text{F})_2\text{CH}_2\text{CH}_2\text{Cl}$, as compared with $\text{C}_2\text{H}_5\text{Si}(\text{Cl})_2\text{CH}_2\text{CH}_2\text{Cl}$, to undergo β -decomposition, which we have noted previously [3]. In the free-radical chlorination of $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ (Cl_2 and ultraviolet radiation; SO_2Cl_2 and benzoyl peroxide) we have a different mechanism with suppression of the tendency for such nucleophilic attack on Si accompanied by electrophilic on the aromatic nucleus.

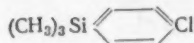
The structures of the chlorination products were proved by confirmatory syntheses and determination of Raman spectra on substances of known structure with subsequent comparison with the spectra of the mixtures. The physical properties of the original substances and some of the chlorination products are given in the table. The following frequencies were found in the spectra of pure samples of o-chlorophenyl-, m-chlorophenyl-, and p-chlorophenyl-trimethylsilanes:



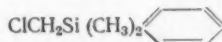
$\nu(\text{cm}^{-1})$: 169(2), 193(4), 217(4), 245(3), 281(2), 328(1), 341(0), 405(4), 442(7), 488(0), 624(10), 662(4), 696(3), 713(2), 736(2), 759(2), 847(2), 980(2), 996(2), 1038(8 db), 1111(5), 1161(4), 1199(0), 1244(3 b), 1418 (3 b), 1558(4), 1580(5), 2895(10), 2955(8), 3054(8).



$\nu(\text{cm}^{-1})$: 191(6), 215(5), 261(5), 326(1), 346(1), 367(2), 393(5), 424(5), 457(0), 566(2), 624(10), 669(5sh), 668(4 b), 757(3), 789(3), 843(3 b), 897(0), 996(10), 1041(3), 1072(5sh), 1093(4), 1115(4), 1130(4), 1168(2), 1193(0), 1245(3 b), 1258(3), 1317(0), 1385(3), 1407(1), 1554(4), 1581(6), 2837(2), 2894(10), 2953(10), 3056(5).















$\nu(\text{cm}^{-1})$: 169(4), 203(6 b), 223(4), 265(2), 323(5), 340(2), 507(3), 632(10), 696(3 b), 741(7), 762(3), 842(3 b), 997(1), 1060(4), 1084(10), 1111(3), 1126(1), 1186(5), 1250(4 b), 1264(2), 1307(2), 1380(2), 1409(4), 1475(0), 1578(10), 2838(1), 2900(10), 2957(10), 3039(1), 3069(3).



$\nu(\text{cm}^{-1})$: 170(0), 212(7), 221(7), 257(1), 369(5), 398(2), 462(3 b), 498(0), 544(1), 604(8 b), 620(6), 650(2), 667(4), 701(5 b), 749(7 b), 793(1), 850(1), 900(1), 944(5), 998(10), 1031(8), 1102(1), 1116(6), 1156(6), 1191(2), 1206(5), 1250(1 b), 1285(0), 1392(3 b), 1486(1), 1567(2), 1588(8), 2898(7 b), 2923(2), 2964(8 b), 2990(1), 3050(6).

In the spectrum of the mixture of chlorination products from $(\text{CH}_3)_3\text{Si}-\text{C}_6\text{H}_5$ we observed all the intense lines of o-, m-, and p-chlorophenyltrimethylsilanes: ortho-193, 217, 405, 442, 624, 1038, 1111, 1558, 1580 cm^{-1} ; meta-424, 666, 996, 1072 cm^{-1} ; para-632, 1060, 1084, 1186 cm^{-1} . Comparison of the intensities of these lines with those of the standards, measured photometrically, enabled us to determine the amount of each isomer in the mixture: ortho 51%; meta 24%; para 25%.

The spectrum of $\text{ClCH}_2\text{Si}(\text{CH}_3)_2-\text{C}_6\text{H}_5$ was found to be identical with that of the product of photochemical chlorination.

Comp. No.	Compound	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR	
					found	calc.
I	 $\text{Si}(\text{CH}_3)_3$	169—170(743)	0,8692	1,4915	50,10	49,95
II	 $\text{Si}(\text{Cl})(\text{CH}_3)_2$	192,5(730,5)	1,0275	1,5052	49,29	49,58
III	 $\text{Si}(\text{Cl})_2(\text{CH}_3)$	203,0(752)	1,1774	1,5185	49,22	49,21
IV	 SiF_3	102—102,5(748,3)	1,2169	1,4110	33,09	31,74
V	 $\text{Si}(\text{CH}_3)_3$	211,0(750,5)	0,9986	1,5085	55,17	54,79
VI	 $\text{Si}(\text{CH}_3)_3$	208,7(745)	1,0121	1,5110	54,67	54,79
VII	 $\text{Si}(\text{CH}_3)_3$	209,4(749,5)	1,0189	1,5150	54,67	54,79
VIII	 $\text{Si}(\text{CH}_3)_2$ CH_2Cl	225,0(748)	1,0261	1,5199	54,71	54,79
IX	 SiCl_3	233,0(745,5)	1,4296	1,5418	54,13	53,68
X	 SiF_3	139,5—140,4(759)	1,3684	1,4430	38,16	36,58
XI	 SiF_3	150—150,5(747,3)	1,3856	1,4460	37,84	36,58
XII	 CH_2SiF_3	134—135(741,5)	1,2107	1,4315	37,70	36,31

EXPERIMENTAL

Preparation of $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ (I), $(\text{CH}_3)_2\text{Si}(\text{Cl})\text{C}_6\text{H}_5$ (II), $(\text{CH}_3)\text{Si}(\text{Cl})_2\text{C}_6\text{H}_5$, p- $\text{ClC}_6\text{H}_4\text{Si}(\text{CH}_3)_3$ (V). The compounds (I), (II), (III), and (V) were prepared by organomagnesium synthesis under the usual conditions from $\text{C}_6\text{H}_5\text{MgBr}$ (I-III) and p- $\text{ClC}_6\text{H}_4\text{MgBr}$, $(\text{CH}_3)_3\text{SiCl}$, $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3 in the following amounts: (I) 281 g (57%); (II) 80 g (24%); (III) 125 g (45%); (V) 30 g (32%). The substances were distilled at least twice through columns.

Preparation of $\text{C}_6\text{H}_5\text{SiF}_3$ (IV). The substance (IV) was prepared from 543 g of $\text{Cl}_3\text{SiC}_6\text{H}_5$ and 430 g of SbF_3 in 47% yield (194 g) (after vacuum fractionation through a column).

Preparation of m- $\text{ClC}_6\text{H}_4\text{Si}(\text{CH}_3)_3$ (VI). The compound (VI) was prepared by the methylation of $\text{Cl}_3\text{SiC}_6\text{H}_4\text{Cl}$ -m (104 g; b.p. $230-231^\circ/751\text{ mm}$), which was isolated from the products of the chlorination of $\text{C}_6\text{H}_5\text{SiCl}_3$ [4] and carefully purified by distillation through a column of 35-40 theoretical plates. After two vacuum distillations through a column the yield of (VI) was 55 g (70%). According to the Raman spectrum it contained neither (V) nor (VII).

Preparation of $o\text{-ClC}_6\text{H}_4\text{Si}(\text{CH}_3)_3$ (VII). The compound was prepared by the methylation of 77 g of trichloro-*o*-chlorophenylsilane, which was isolated by careful distillation of the products of the chlorination of $\text{Cl}_3\text{SiC}_6\text{H}_5$ [4]. After vacuum distillation and two fractionations through a column, we obtained 32 g (55%) of (VII).

Preparation of $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Cl}$ (VIII). The compound (VIII) was prepared from $\text{C}_6\text{H}_5\text{MgBr}$ (157 g of $\text{C}_6\text{H}_5\text{Br}$) and 143 g of chloro(chloromethyl)dimethylsilane in ether. The reaction products were decomposed with water, the ether solution was dried over sodium sulfate, and ether was distilled off. After vacuum distillation and two fractionations through a column we obtained 20.4 g (12%) of (VIII). When the procedure was modified somewhat (no decomposition of the products with water), we obtained 32.6 g of $(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{Cl})\text{SiC}_6\text{H}_5$, an isomerization product from (VIII) (according to the Raman spectrum); b.p. 212.5° (751 mm); d_4^{20} 1.0160; n_D^{20} 1.5100; found MR 54.21; calculated MR 54.37.

Preparation of $p\text{-ClC}_6\text{H}_4\text{SiCl}_3$ (IX). The substance (IX) was prepared from 195 g of $p\text{-ClC}_6\text{H}_5\text{Br}$, 24 g of magnesium, and 360 g of SiCl_4 under the previously described conditions [5]. After distillation through a column we obtained 34 g of (IX).

Preparation of $m\text{-ClC}_6\text{H}_4\text{SiF}_3$ (X) and $o\text{-ClC}_6\text{H}_4\text{SiF}_3$ (XI) by the Chlorination of $\text{C}_6\text{H}_5\text{SiF}_3$ (IV). The substance (IV) (165.2 g) was chlorinated in presence of iron filings (0.84 g) at $50\text{--}55^\circ$ for 23 hours in a flask fitted with a reflux condenser; 183.7 g of chlorination products was distilled at 160 mm; 178.7 g of the distillate was fractionated through a column. We obtained: 1) 30.7 g of unchanged (IV) (b.p. $102\text{--}102.5^\circ/749.6$ mm); 2) 65.2 g of (X) (the spectrum of methylated (X) was identical with the spectrum of (VI)* with admixture of (V) in an amount not greater than 5%); 3) 14.2 g of (XI)**; 4) 14.8 g of *p*-dichlorobenzene (b.p. $173.5^\circ/759$ mm). The proportions of isomers were $o : m : p = 18 : 79 : 3$. In another experiment in which 193 g of (IV) was chlorinated, (X) and (XI) were obtained in yields of 18.8 g and 4.2 g, respectively. According to the Raman spectra and the fractionation results the proportions of isomers were $o : m : p = 18 : 82 : 0$.

Chlorination of $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ (I). The compound (I) was chlorinated by two methods:

a) The compound (I) (112.8 g) was chlorinated in presence of iron powder (0.57 g) for 2 hours 15 minutes at about 50° . This gave 135.2 g of chlorination products, which were first vacuum-distilled (27–159 mm). From 117 g of distillate, fractionation through a column gave: 1) 26.6 g of $(\text{CH}_3)_3\text{SiCl}$ (b.p. $56.6^\circ/747.2$ mm); 2) 5.5 g of benzene (b.p. $78\text{--}80^\circ$); 3) 19.6 g of chlorobenzene (b.p. $131.5^\circ/747.2$ mm); 4) 56.6 g of unchanged (I) (b.p. $170\text{--}170.5^\circ$); 5) 4.1 g of a mixture of (V), (VI), and (VII), b.p. $208.3\text{--}208.5^\circ$ (747 mm), d_4^{20} 1.0100; n_D^{20} 1.5122. Results of spectrum analysis of the mixture: 25% of (V), 24% of (VI), and 51% of (VII). In another experiment 127 g of (I) gave 19.2 g of a mixture of (V), (VI), and (VII). The proportions of isomers were the same.

b) The compound (I) (72 g) was chlorinated photochemically under the conditions described previously [2, 3, 5] for 16 hours (until the temperature in the still reached 200°); 78.2 g of the reaction products were vacuum-distilled (19 mm) and then fractionated through a column. We isolated: 1) 20.5 g of unchanged (I); 2) 21.7 g of (VIII); b.p. $224.5\text{--}225.3^\circ$ (741 mm); d_4^{20} 1.0271; n_D^{20} 1.5195. The structure of the product of the photochemical chlorination of (I) was proved to be identical with that of (VIII) (above-given constants, and also the Raman spectra)***.

* $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{Cl-m}$ with admixture of $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{Cl-p}$ (not more than 5%) prepared in 75% (48.6 g) yield by the methylation of $\text{F}_3\text{SiC}_6\text{H}_4\text{Cl-m}$ had the following constants: b.p. 208.4° (745 mm), d_4^{20} 1.0038; n_D^{20} 1.5095; found MR 54.98; calculated MR 54.79.

** The structure of $\text{F}_3\text{SiC}_6\text{H}_4\text{Cl-o}$ was proved by methylation and comparison of the properties (Raman spectrum, physical properties) of the $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{Cl-o}$ with those of authentic (VII). The yield of (VII) in the methylation of $\text{F}_3\text{SiC}_6\text{H}_4\text{Cl-o}$ was 52% (9.5 g); b.p. 209.4° (749.5 mm); d_4^{20} 1.0182; n_D^{20} 1.5152; found MR 54.72; calculated MR 54.79.

*** The same results were obtained in the chlorination of 39.5 of (I) with 35 g of SO_2Cl_2 in presence of 0.34 g of benzoyl peroxide (10 hours). Vacuum fractionation and fractionation through a column gave 8.3 g of (VIII); b.p. 225° (748 mm); d_4^{20} 1.0293; n_D^{20} 1.5185.

Chlorination of $\text{Cl}-\text{C}_6\text{H}_4-\text{Si}(\text{Cl})_3$ (IX). The compound (IX) (58.3 g) was chlorinated in presence of

iron powder (0.29 g) for 9.5 hours. From 65.7 g of chlorination products we obtained 57.1 g by vacuum-distillation, and the distillate was fractionated through a column. We isolated: 1) 10.6 g of unchanged (IX); 2) 26.8 g of trichloro(dichlorophenyl)silanes, b.p. 263° (733.5 mm), d_4^{20} 1.5409, and n_D^{20} 1.5610, which, according to spectrum analysis, consisted of a mixture of the 2,4- and 3,4-dichlorophenyl compounds. The same results were obtained in the chlorination of 133.3 g of (IX) in presence of 0.65 g of iron powder at 70° , when, after vacuum distillation and fractionation through a column, we obtained 117 g of a mixture of trichloro(dichlorophenyl)silanes; b.p. $263.7-265^\circ$ (752.5 mm); d_4^{20} 1.5409-1.5481; n_D^{20} 1.5610-1.5615.

Chlorination of $\text{Cl}_3\text{SiC}_6\text{H}_5$ to Trichloro(dichlorophenyl)silanes. In the chlorination of $\text{Cl}_3\text{SiC}_6\text{H}_5$ in presence of iron filings it was noted that in some cases, when the increase in weight was more than that required for chlorination to monochloro compounds, there was a considerable reduction in the amount of trichloro(o-chlorophenyl)silane and a simultaneous increase in the amount of dichloro compounds. Thus, in the chlorination of 487 g of $\text{C}_6\text{H}_5\text{SiCl}_3$ we obtained 619 g of chlorination products. Fractionation of 352 g of these through a column gave: 1) 80 g of a mixture of trichloro(m-chlorophenyl)- and trichloro(p-chlorophenyl)-silanes; 2) a very small amount of trichloro(o-chlorophenyl)silane; 3) 119 g of trichloro(dichlorophenyl)silanes; b.p. $264.5-265.5^\circ$ (746 mm); d_4^{20} 1.5506; n_D^{20} 1.5650. The Raman spectrum of the mixture of trichloro(dichlorophenyl)silanes of b.p. $264.5-265.5^\circ$ was not identical with that of the mixture of the 2,4 and 3,4 isomers obtained in the preceding experiment from (IX), though these isomers were undoubtedly present; 4) 6 g of trichloro(dichlorophenyl)silanes of b.p. $273.7-274^\circ$ (757 mm), d_4^{20} 1.5619, and n_D^{20} 1.5655, the structures of which were not established.

Bromination of $\text{F}_3\text{Si}-\text{C}_6\text{H}_4-$. Bromine (222.2 g) was added to a mixture of 225 g of $\text{F}_3\text{Si}-\text{C}_6\text{H}_4-$ and 1.12 g of iron powder. When dropping had continued for 20 minutes, vigorous liberation of F_3SiBr began at $31-33^\circ$. Further reaction was carried out at 20° . After vacuum distillation and fractionation through a column, 256 g of reaction products gave: 1) 122 g of $\text{Br}-\text{C}_6\text{H}_4-\text{Br}$; m.p. $87.5-88^\circ$; 2) 53.1 g of unchanged $\text{F}_3\text{Si}-\text{C}_6\text{H}_4-$; 3) 9.3 g (3.6%) of $\text{BrC}_6\text{H}_4\text{SiF}_3$; b.p. $95-98^\circ$ (125 mm); n_D^{20} 1.4762; d_4^{20} 1.6516.

Bromination of $\text{F}_3\text{Si}-\text{C}_6\text{H}_3\text{Cl}-$ Bromine (27.6 g) was added to a mixture of 33.8 g of $\text{F}_3\text{Si}-\text{C}_6\text{H}_3\text{Cl}-$ and 0.17 g of iron powder. The reaction was carried out at 30° . After vacuum distillation and fractionation through a column, 40.7 g of reaction products gave: 1) 4.1 g of unchanged m- $\text{ClCH}_2\text{SiF}_3$; 2) 6.1 g (14%) of m- $\text{ClBrC}_6\text{H}_3\text{SiF}_3$, b.p. 194° (754.2 mm), n_D^{20} 1.5023; d_4^{20} 1.7335; 3) 6.6 g of a crystalline substance of unknown structure.

Bromination of $(\text{CH}_3)_3\text{Si}-\text{C}_6\text{H}_4-$ Bromine (58 g) was added dropwise to a mixture of 0.27 g of iron powder and 56 g of $(\text{CH}_3)_3\text{Si}-\text{C}_6\text{H}_4-$. The reaction started at 43° and was carried out at $45-50^\circ$. We obtained 112 g of reaction products, and distillation of these through a column and in a vacuum gave: 1) 52.8 g (92%) of $(\text{CH}_3)_3\text{SiBr}$, b.p. 32° (133 mm), n_D^{20} 1.4270; d_4^{20} 1.1853. 2) 51 g of (87%) of $\text{Br}-\text{C}_6\text{H}_4-$, b.p. 72° (50 mm), n_D^{20} 1.5591; d_4^{20} 1.4953.

Bromination of $\text{F}_3\text{SiCH}_2-\text{C}_6\text{H}_4-$ Bromine (48 g) was added dropwise to a mixture of 0.26 g iron powder and 5.3 g of $\text{F}_3\text{SiCH}_2-\text{C}_6\text{H}_4-$. The reaction temperature was 25° . A small portion of the reaction products (evidently SiF_3Br) was collected in a trap. The rest (74 g) consisted of crystals, and vacuum distillation of these gave 56.9 g (76%) of (bromobenzyl) trifluorosilane, b.p. $105-106^\circ$ (14 mm), which was treated with $\text{C}_2\text{H}_5\text{MgBr}$.

Treatment of the reaction products with water, followed by drying and vacuum distillation, gave 44.7 g of a (bromobenzyl) trifluorosilane, which, according to the Raman spectrum, was almost pure (p-bromobenzyl) trifluorosilane. Found: C 32.69; 32.73; H 2.62; 2.45; Si 10.83; 10.85; Br 31.23; 31.35; F 22.38; 22.36%. $\text{C}_7\text{H}_6\text{SiBrF}_3$. Calculated: C 32.96; H 2.37; Si 11.00; Br 31.33; F 22.34%.

SUMMARY

1. In the chlorination of $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ and $\text{F}_3\text{SiC}_6\text{H}_5$ in presence of iron, the trimethylsilyl group is ortho-para orienting and the trifluorosilyl group is powerfully meta orienting.
2. In the chlorination of phenylsilanes the replacement of alkyl groups attached to the silicon by the more highly electronegative chlorine or fluorine atoms leads to change from ortho-para orientation to meta orientation. The dichlorination of $\text{Cl}_3\text{SiC}_6\text{H}_5$ and of $p\text{-ClC}_6\text{H}_4\text{SiCl}_3$ results in the formation of a complex mixture of reaction products.
3. Unlike chlorination in presence of iron powder, photochemical chlorination of $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ occurs only at the C-H bonds of the methyl groups.
4. Unlike the trichlorosilyl group, the trifluorosilyl groups and other groups directly attached to the aromatic nucleus are fairly readily eliminated during halogenation in presence of iron powder, which is evidently associated with the steric and induction effects of groups attached to silicon, with the electrophilic character of the silicon, and also with the ionic mechanism of the reactions.

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SYNTHETIC ANESTHETICS

COMMUNICATION 30. SYNTHESIS AND STUDY OF p-METHOXY- AND p-CHLORO- α -(2-DIMETHYLAMINOETHYL) BENZYL ALCOHOLS AND THEIR ESTERS

I. N. Nazarov and E. M. Cherkasova

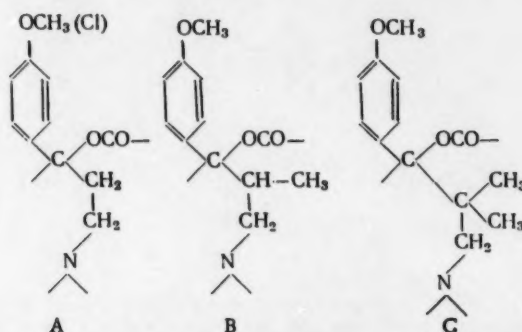
M. V. Lomonosov Institute of Fine Chemical Technology

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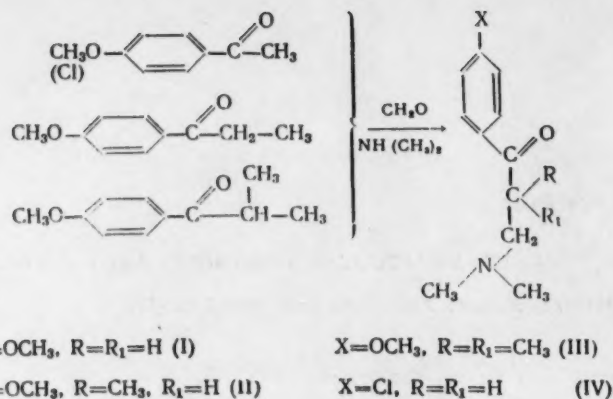
Original article submitted July 2, 1958

In recent years in our laboratory we have synthesized various esters of phenyl alkylamino alcohols, and some of these have been found to have considerable physiological activity [1]. In all the substances synthesized the phenyl group was unsubstituted. In continuing these investigations, we considered it to be of interest to determine the effect of substituents in the phenyl nucleus, particularly the p-methoxy group, on the chemical and pharmacological behavior of these types of organic substances. There is reason to suppose that such substituents will have a favorable effect, as shown recently in a less complicated case [2]. However, the opposite effect has been obtained, e.g., in the amides of β -alkylamino acids [3]. In the case of the esters of 2-morpholino-1-propanols [4] this sort of substitution is almost without effect. We considered also that, in view of the above considerations, it would be of interest to prepare compounds of these types containing a p-chlorophenyl group.

In the present paper we describe ways of synthesizing esters of three types of p-methoxy- and p-chloro- α -(2-dimethylaminoethyl)benzyl alcohols in which the 2-dimethylaminoethyl group (A) is unsubstituted, (B) has a 1-methyl substituent, and (C) has 1,1-dimethyl substituents.

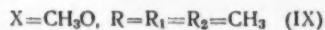
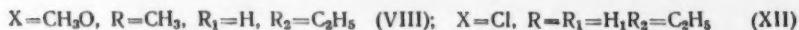
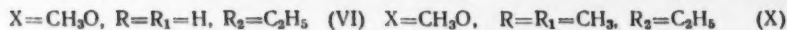
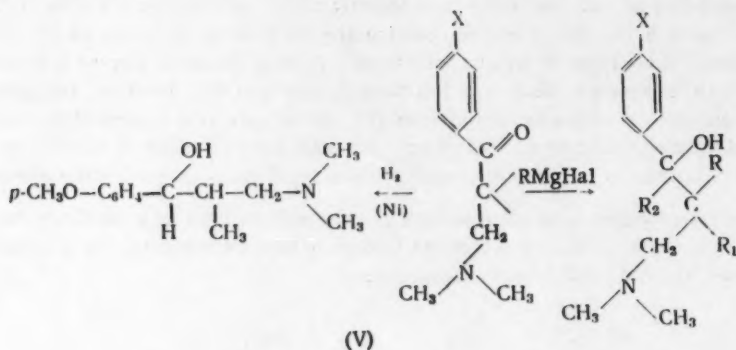


The starting materials for the synthesis of these compounds were 4'-methoxy(or 4' -chloro)-acetophenone, 4' -methoxypropiofenone, and 4' -methoxyisobutyrophenone, which were converted by the Mannich reaction into the amino ketones (I)-(IV):



In this reaction there is a definite orientation of substitution. The yields of the amino ketones (I)-(III) fell rapidly as the number of methyl substituents increased (from 90% to 16%, see Table 1). The highest yield of amino ketone (III) was attained when the ion-exchange resin KU-1 was present; in absence of this, yields of not greater than 10% were obtained in numerous experiments (about 30) under various conditions.

New tertiary alcohols were obtained by reaction of organomagnesium compounds with the amino ketones, and by catalytic reduction a secondary amino alcohol (V) was obtained:



As a result of the investigation of this reaction, the desired amino alcohols were obtained (30-78% yield) with the exception of α -(2-dimethylaminoethyl)-*p*-methoxy- α -methylbenzyl alcohol (XIII). It was found that in the process of reaction of the amino ketone (I) with CH_3MgI , CH_3MgBr , or even CH_3Li almost complete enolization of (I) occurs. Special experiments in which the gases liberated were analyzed, showed that the amino ketone (I) undergoes 90% enolization in presence of CH_3MgI . The amino alcohol (XIII) was prepared in 41% yield by the following reaction:

TABLE 1 Amino ketones

$$\begin{array}{c}
 \text{O} \quad \text{R} \\
 \parallel \quad | \\
 \text{X}-\text{C}_6\text{H}_4-\text{C}-\text{CH}_2-\text{N}(\text{CH}_3)_2 \\
 | \\
 \text{R}_1
 \end{array}$$

Com- pound	X	R	R ₁	B.p. of base in °C (p in mm)	Yield (%)	Found (%)			Calculated (%)			Found (%)			Calculated (%)		
						C	H	N	C	H	N	N	Cl	Cl	N	Cl	Cl
(I) [5]	CH ₃ O	H	H	—	—	—	—	—	—	—	—	—	14,65	—	—	14,55	—
(II)	CH ₃ O	CH ₃	H	155—158(7)	49	—	5,80 5,90	—	—	—	6,3	5,1 5,3	—	—	5,44	—	—
(III)	CH ₃ O	CH ₃	CH ₃	122—125(2)	16*	71,54 71,80	8,63 9,11	5,70 5,80	71,5	8,95	5,96	4,91 5,09	—	—	5,14	—	—
(IV) [6]	Cl	H	H	—	—	—	—	—	—	—	—	5,40 5,37	—	—	5,63	—	—
CH ₃ COCH ₂ CH ₂ N(CH ₃) ₂ [7]				51—53(15)	11,3	—	—	—	—	—	—	—	—	—	—	—	—

* 52% on the 4'-methoxyisobutyrophenone that reacted.

TABLE 2 Amino alcohols

$$\begin{array}{c}
 \text{CH}_3 \\
 | \\
 \text{X} - \text{C}_6\text{H}_4 - \text{C} \begin{array}{l} \nearrow \text{OH} \nearrow \text{R} \\ \searrow \text{C-CH}_2\text{-N} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{R}_1 \end{array} \end{array} \\
 | \\
 \text{R}_2
 \end{array}$$

Compound	X	R	R ₁	R ₂	B.p. in °C (p in mm)	M.p. (°C)	Yield (%)	Found (%)			Calculated (%)			M.p. of hydrochloride (°C)	N found (%)	N calc. (%)	Active hydrogens N % found	N % calc.
								C	H	N	C	H	N					
(V)	CH ₃ O	CH ₃	H	H	—	78—79	29.4	70.29 70.24	9.28 9.14	5.96 5.88	71.0	9.42	6.28	166—167	5.20 5.67	5.40	0.89	1
(VI)	CH ₃ O	H	H	C ₂ H ₅	140—142(4)	86—88	77.5	71.12 71.19	9.54 9.45	5.89 5.74	70.8	9.7	5.90	159—160	5.49 5.45	5.14	0.93	1
(VII)	CH ₃ O	CH ₃	H	CH ₃	105—108(2)	49—50	71.2	—	—	5.53 5.56	—	—	5.90	168—169	4.96 4.91	5.14	0.81	1
(VIII)*	CH ₃ O	CH ₃	H	C ₂ H ₅	112—115(2)	—	75.4	72.16 72.21	9.64 9.60	5.90 5.94	71.9	9.95	5.59	175—176	5.16 4.87	4.89	1.09	1
(IX)	CH ₃ O	CH ₃	CH ₃	CH ₃	152—154(4)	—	71.1	—	—	5.78 5.81	—	—	5.59	Hygroscopic crystals whose m.p. we could not determine				—
(X)	CH ₃ O	CH ₃	CH ₃	C ₂ H ₅	165—170(5)	—	68.1	72.54 72.70	9.9 9.5	5.04 5.00	72.5	10.2	5.29	185—188	4.25 4.20	4.65	0.88	1
(XI)	Cl	H	H	CH ₃	125—128(5)	43—44	53.0	—	—	6.50 6.52	—	—	6.15	164—166	5.48 5.22	5.31	—	—
(XII)	Cl	H	H	C ₂ H ₅	120—122(2)	44—45	63.0	—	—	5.40 5.45	—	—	5.8	167—169	4.99 4.93	5.02	—	—
(XIII)**	CH ₃ O	H	H	CH ₃	122—123(2.5)	—	40.8	69.95 69.71	9.35 9.16	6.30 6.37	69.8	9.41	6.27	204—205	5.75 5.80	5.41	0.94	1

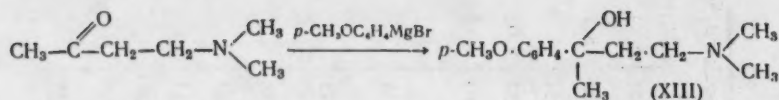
* n_D^{20} 1.5205; d_4^{20} 1.019; found MR 74.94; calculated MR 74.97.

** n_D^{20} 1.5713; d_4^{20} 1.032; found MR 65.42; calculated MR 65.71.



Com- pound	X	R	R ₁	R ₂	R ₃	M.p. of hydrochloride (°C)	Yield (%)	Found (%)		Calculated (%)	
								N	Cl	N	Cl
(XIV)	CH ₃ O	H	H	C ₂ H ₅	C ₆ H ₅	131-132, 5	18, 6	3, 65	9, 62	3, 71	9, 42
(XV)	CH ₃ O	H	H	C ₂ H ₅	C ₆ H ₅ OCH ₂	80-83	Max. 100	3, 66	8, 72	3, 44	8, 7
(XVI)	CH ₃ O	CH ₃	H	H	C ₆ H ₅	174-175	57, 5	3, 64	—	3, 84	—
(XVII)	CH ₃ O	CH ₃	H	H	C ₆ H ₅ OCH ₂	153-154	58, 8	4, 12	—	—	—
(XVIII)	CH ₃ O	CH ₃	H	H	C ₆ H ₅ CH = CH	103-105	51, 1	3, 95	8, 82	3, 57	9, 04
(XIX)	CH ₃ O	CH ₃	H	C ₂ H ₅	C ₆ H ₅ CH = CH	130-132	48, 2	3, 90	9, 23	3, 60	9, 13
(XX)	CH ₃ O	CH ₃	CH ₃	CH ₃	p-CH ₃ OC H ₄ OCH ₂	M.p. of base* 92-94 M.p. of methiodide 184-186	31, 4 (base)	3, 71 3, 47 3, 36 3, 58 3, 67 (base)	—	3, 36	—
(XXI)	CH ₃ O	CH ₃	CH ₃	CH ₃	C ₆ H ₅ CH = CH	148-150	39, 7	2, 35 2, 62 (methiodide)	—	2, 48	—
(XXII)	CH ₃ O	CH ₃	CH ₃	C ₂ H ₅	C ₆ H ₅	146-148	15	3, 70 3, 71 3, 75	—	3, 43	—
(XXIII)	CH ₃ O	CH ₃	CH ₃	C ₂ H ₅	C ₆ H ₅ OCH ₂	132-135	56, 8	3, 55 3, 58 3, 80	—	3, 21	—
(XXIV)	Cl	H	H	C ₂ H ₅	C ₆ H ₅	162-164	66, 3	3, 64	—	3, 66	—
(XXV)	Cl	H	H	C ₂ H ₅	C ₆ H ₅ CH = CH	176-178	51, 1	3, 71 3, 74 3, 39 3, 49	—	3, 42	—
(XXVI)	Cl	H	H	C ₂ H ₅	C ₆ H ₅ OCH ₂	157-159	77, 8	—	—	3, 38	—

* After 50 hours (XV) was partially hydrolyzed; the nitrogen content rose to 4.45-4.50%.



It should be noted that the catalytic hydrogenation of (I) and (III) did not lead to the expected alcohols, whereas analogous amino ketones containing an unsubstituted phenyl group are reduced smoothly [8]. This would appear to be due to the unfavorable effect of the *p*-methoxyphenyl group. The results of experiments on amino alcohols are collected in Table 2.

By the esterification of the alcohols (V), (VI), (X), and (XII) with benzoyl chloride and phenoxyacetyl chloride, we obtained the corresponding benzoic esters (XVI), (XIV), (XXII), and (XXIV) and phenoxyacetic esters (XVII), (XV), (XIII), and (XXVI). By the action of cinnamoyl chloride on the alcohols (V), (VIII), (IX), and (XII), we obtained the cinnamic esters (XVIII), (XIX), (XXI), and (XXV), and the (*p*-methoxyphenoxy) acetic ester (XX) was synthesized from the amino alcohol (IX) and (*p*-methoxyphenoxy)acetyl chloride. It should be noted that the acylation of the tertiary α -alkyl- α -(2-dimethylaminoethyl)-*p*-methoxybenzyl alcohols does not generally go so readily as that of their analogs in which the nucleus is unsubstituted. This is particularly true for the amino alcohols in which the 2-dimethylaminoethyl group is unsubstituted, i.e., (VI) and (XIII). Moreover, the ester (XV) hydrolyzes on standing to the original alcohol (Table 3). In all cases (except XX), the esters were isolated as readily crystallizing colorless hydrochlorides, which were soluble in water; they were subjected to pharmacological investigation, the results of which will be published. The amino ketone (II) and the amino alcohol (VI) were shown by special experiments at the Rubber Technology Department of the Institute of Fine Chemical Technology to be effective vulcanization accelerators for rubber [9].

EXPERIMENTAL

The β -amino ketones were synthesized by the Mannich reaction (See Table 1). We describe the preparation of (III), which has not been described in the literature.

3-Dimethylamino-4'-methoxy-2,2-dimethylpropiofenone (III). A mixture of 65.2 g of 4'-methoxyisobutyrophenone*, 36.3 g of dimethylamine hydrochloride, 29.4 g of paraform, 85 ml of benzene, and 2.18 g of the cation-exchange resin KU-1 was heated in a boiling water bath for four hours with vigorous stirring. On the next day benzene was distilled off at the water pump, the residue was treated with 1 : 1 hydrochloric acid, and the neutral products were extracted with ether and dried. We obtained 45.4 g of unchanged 4'-methoxyisobutyrophenone b.p. 131-134° (7 mm). The acidic aqueous layer was saturated with sodium carbonate, and the oil that rose to the surface was extracted with ether, dried with magnesium sulfate, and distilled to remove ether. Vacuum fractionation of the residue gave 13.7 g (16%) of 3-dimethylamino-4'-methoxy-2,2-dimethylpropiofenone (III), b.p. 122-125° (2 mm). Found: C 71.54; 71.80; H 8.63; 9.11; N 5.70; 5.80%. $\text{C}_{14}\text{H}_{21}\text{O}_2\text{N}$. Calculated: C 71.50; H 8.95; N 5.96%.

The hydrochloride of (III) was prepared by the passage of dry hydrogen chloride through a solution of the amino ketone in chloroform; m.p. 146-148° (from absolute alcohol). Found: N 4.91; 5.09%. $\text{C}_{14}\text{H}_{21}\text{O}_2\text{NHCl}$. Calculated: N 5.14%.

The amino alcohols were prepared by a general method. By way of example, we describe the synthesis of the secondary alcohol (V) and of the tertiary alcohol (VIII).

α -(2-Dimethylaminoethyl)-*p*-methoxybenzyl Alcohol (V). The amino ketone (II) (2.2 g), as a solution in 25 ml of absolute ethanol, was hydrogenated at room temperature in presence of Raney nickel and palladium catalysts. The amount of hydrogen absorbed was 300 ml. The catalysts were filtered off, solvent was distilled off, and the residue solidified. We obtained 0.65 g (29.4%) of α -(2-dimethylaminoethyl)-*p*-methoxybenzyl alcohol (V), m.p. 78-79° (from gasoline). Found: C 70.29; 70.24; H 9.28; 9.14; N 5.96; 5.88% active hydrogens 0.89. $\text{C}_{13}\text{H}_{21}\text{ON}$. Calculated: C 70.0; H 9.42; N 6.28%; active hydrogens 1.

The hydrochloride melted at 166-167°. Found: N 5.20; 5.67%. $\text{C}_{13}\text{H}_{21}\text{ONHCl}$. Calculated: N 5.40%.

* This was prepared in 98% yield from anisole and isobutyryl chloride in CCl_4 in presence of AlCl_3 . The yield is not stated in the literature [10].

α -Ethyl- α -(2-dimethylamino-1-methylethyl)-p-methoxybenzyl Alcohol (VIII). Gradual addition was made of 15 g of 3-dimethylamino-4'-methoxy-2,2-dimethylpropiophenone hydrochloride [hydrochloride of (III)] to a solution of ethylmagnesium bromide (prepared from 7.2 g of magnesium and 31.8 g of ethyl bromide in 80 ml of dry ether) with vigorous stirring at from -8° to -10° . When the whole of the amino ketone had been added, stirring was continued for one hour at room temperature. On the next day, the mixture was heated for two hours at the boiling point of ether; the product was hydrolyzed with 1 : 1 hydrochloric acid with application of cooling, and the neutral products were extracted with ether and separated. The aqueous layer was saturated with sodium carbonate, the oil that separated was repeatedly extracted with ether, ether was distilled off, and the residue was fractionated. We obtained 11 g (75.4%) of α -ethyl- α -(dimethylamino-1-methylethyl)-p-methoxybenzyl alcohol (VIII); b.p. $112-115^{\circ}$ (2 mm); n_D^{20} 1.5205; d_4^{20} 1.019; found MR 74.94; calculated MR 74.97. Found: C 72.16; 72.21; H 9.64; 9.60; N 5.90; 5.94%. $C_{15}H_{25}ON$. Calculated: C 71.9; H 9.95; N 5.59%. Active hydrogens—found 1.09; calculated 1.

The hydrochloride melted at $175-176^{\circ}$. Found: N 5.16; 4.87%. $C_{15}H_{25}ON \cdot HCl$. Calculated: N 4.89%.

In most experiments the esters of the amino alcohols were obtained as hydrochlorides directly in the course of the reaction; in one case the free base was obtained. We describe typical examples.

α -(2-Dimethylamino-1-methylethyl)-p-methoxybenzyl Alcohol Phenoxyacetic Ester (XVII). With water cooling a solution of 1.7 g of phenoxyacetyl chloride in 6 ml of benzene was added to 1.1 g of the amino alcohol (V) and 0.1 g of magnesium in 12 ml of dry benzene. The precipitate formed was washed several times with dry ether until the odor of the acid chloride was removed, and it was then repeatedly crystallized from an acetone-alcohol mixture. We obtained 1.14 g (58.8%) of the hydrochloride of α -(2-dimethylamino-1-methylethyl)-p-methoxybenzyl alcohol phenoxyacetic ester (XVII), m.p. $153-154^{\circ}$. Found: N 3.95; 3.90; Cl 8.82%. $C_{21}H_{27}O_4N \cdot HCl$. Calculated: N 3.57; Cl 9.04%.

α -(2-Dimethylamino-1,1-dimethylethyl)-p-methoxy- α -methylbenzyl Alcohol (p-Methoxyphenoxy) acetic Ester (XX). A mixture of 1.6 g of the amino alcohol (IX), 2.2 g of (p-methoxyphenoxy) acetyl chloride, 0.09 g of magnesium, and 10 ml of dry benzene was heated for three hours at 80° with passage of a stream of dry nitrogen. Benzene was vacuum-distilled off, aqueous sodium carbonate solution was added to the residue, and the oil that separated was extracted three times with ether and dried with magnesium sulfate. Ether was distilled off, and the residue solidified. We obtained 0.83 g (31.4%) of α -(2-dimethylamino-1,1-dimethylethyl)-p-methoxy- α -methylbenzyl alcohol (p-methoxyphenoxy)acetic ester (XX), m.p. $92-94^{\circ}$ (from acetone and gasoline). Found: N 3.58; 3.67%. $C_{24}H_{33}O_5N$. Calculated: N 3.38%.

The methiodide melted at $184-186^{\circ}$ (from alcohol). Found: N 2.36; 2.62%. $C_{25}H_{36}O_5NI$. Calculated: N 2.48%.

SUMMARY

1. For the purpose of pharmacological investigation a series of amino alcohols and their esters containing p-methoxy- and p-chloro-phenyl groups was synthesized for the first time.
2. The presence of a methoxy group has an unfavorable effect on the esterification reaction.
3. The amino ketone (II) and the amino alcohol (VI) were found to be effective secondary accelerators for the vulcanization of rubber.

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SYNTHESIS OF DIENES IN WHICH THE DOUBLE BONDS ARE IN FIXED POSITIONS

COMMUNICATION 3. CISOID DIENES*

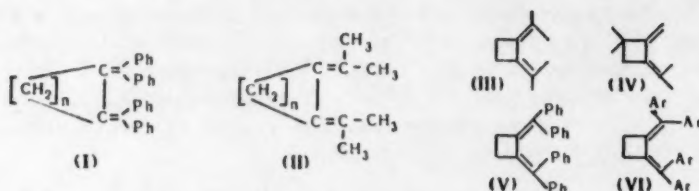
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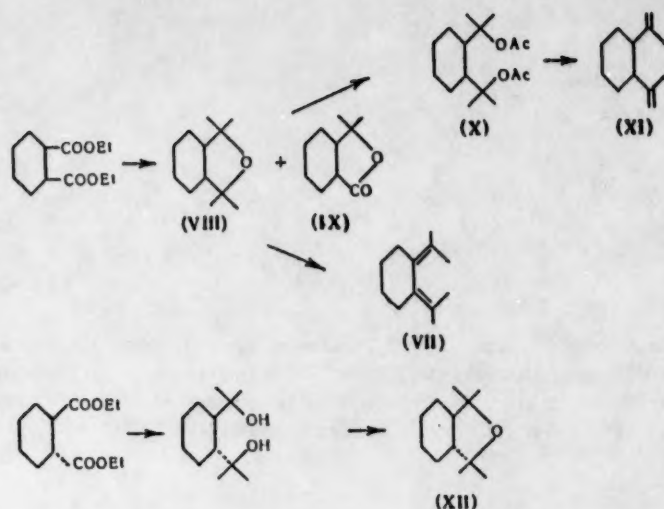
In continuation of our investigations on the synthesis of dienes in which the double bonds are in fixed positions, we attempted to prepare some dienes of the dimethylenecycloalkane type. Such dienes were recently prepared by various workers [1-4] and found to be extremely reactive and to undergo the diene condensation with ease. It was considered to be particularly interesting to develop methods of synthesizing dimethylenecycloalkanes having substituents at the ends of the diene bonds [(I) and (II)].



It is known that aliphatic dienes of this type (2,5-dimethyl-2,4-hexadiene, 1,1,4,4-tetraphenyl-1,3-butadiene) either do not undergo diene condensation [5], or undergo preliminary isomerization with displacement of the double bonds [6]. It was therefore of interest to study the reactivities of dienes of types (I) and (II), which may have a greater tendency to undergo diene condensation than their aliphatic analogs because their double bonds are fixed in the cis position. We succeeded in improving the method of synthesizing 3-methyl-1,2-butadiene [7, 8], and we studied its thermal dimerization. The resulting dimers (III) and (IV) had similar constants to those of the substances isolated by Lebedev [9], and their structures were proved by permanganate oxidation. Neither of these dimers (III) and (IV) gave a crystalline product with maleic anhydride below 100°, and at higher temperatures, reaction was accompanied by opening of the cyclobutane ring [3].

Similar cisoid dienes having terminal phenyl groups (V) and (VI) were prepared recently [10, 11], and they also were found to be unable to undergo diene condensations with maleic anhydride and benzoquinone [12]. Another object of our investigation was the synthesis of 1,2-diisopropylidenecyclohexane (VII), for the preparation of which we followed the following scheme:

*Communication 1, *Doklady Akad. Nauk SSSR* **111**, 358 (1956) [Original Russian pagination. See C. B. Translation].
Communication 2, *Zhur. Obshchei Khim.* **29**, 767 (1959) [Original Russian pagination. See C. B. Translation].



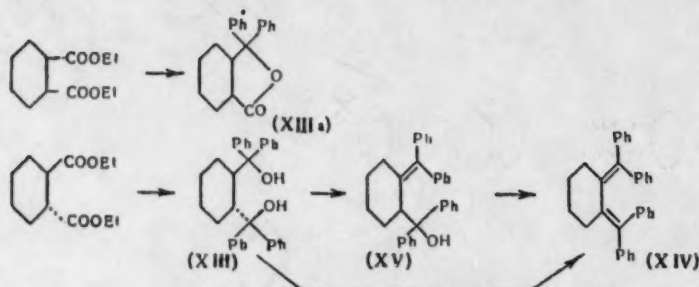
It was found that, unlike the corresponding reaction with a *cis*-cyclobutanedicarboxylic ester [10] reaction of methylmagnesium iodide with diethyl *cis*-1,2-cyclohexanedicarboxylate [13] gives not the diol, but the tetrahydrofuran (VIII) (see [14]). In this reaction a small amount of the lactone (IX) was also isolated. With the object of synthesizing 1,2-diisopropylidenecyclohexane (VII), we studied the catalytic dehydration of the *cis*-tetrahydrofuran (VIII) over various catalysts (alumina, aluminum phosphate, magnesium sulfate, etc.). It is known from the literature [15-17] that the dehydration of tetrahydrofurans does not go readily, though the preparation of dienes in this way has been described in patents. After several unsuccessful attempts, we succeeded in developing a relatively convenient method for the dehydration of the *cis*-tetrahydrofuran (VIII): treatment over alumina in a stream of hydrogen sulfide [18]. The yield of diene fraction was then 50%. On ozonization, the diene (VII) gave acetone and adipic acid. It was found that, like 1,2-diisopropylidenecyclobutane (III), the diene (VII) does not undergo diene condensation with maleic anhydride and with benzoquinone at temperatures up to 100-120°.

We studied also the cleavage of the *cis*-tetrahydrofuran (VIII) with acetic anhydride in presence of zinc chloride [19]. It was found that the diacetic ester (X) then formed was fairly readily converted into 1,2-diisopropenylcyclohexane (XI) by passage through a glass tube heated to 450°; in the ozonization of (XI) formaldehyde and adipic acid were isolated.

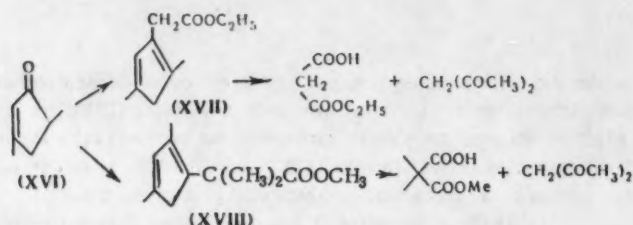
When a Grignard reagent was caused to react with a *trans*-1,2-cyclohexanedicarboxylic ester, instead of with the corresponding *cis*-ester, the expected diol was obtained; reaction with methylmagnesium bromide gave the *trans*-diol, which we did not succeed in obtaining in a crystalline state; in attempts to purify it by distillation it was readily converted into the *trans*-tetrahydrofuran (XII) [20, 21], and this transformation went most readily in presence of potassium hydrogen sulfate or *p*-toluenesulfonic acid.

Reaction of phenylmagnesium bromide with *cis*-1,2-cyclohexanedicarboxylic ester gave a mixture of products, from which only the lactone (XIIIa) was isolated (yield 25%) [12].

Reaction of phenylmagnesium bromide with *trans*-1,2-cyclohexanedicarboxylic ester led to the *trans*-diol (XIII), which was previously prepared by Wittig by reaction of the *trans*-ester with phenyllithium [22]. The resulting diol (XIII) is always contaminated with a small amount of dehydration products, which are very difficult to remove; In our experiments the crude diol was taken for dehydration. Depending on the duration of the reaction, the dehydration of the *trans*-diol (XIII) with a mixture of acetic and hydrochloric acids leads either to the diene (XIV) or to the unsaturated alcohol (XV) which is readily converted into the diene (XIV). The structures of the products isolated were proved by ozonization. Like its cyclobutane analog [12], the diene (XV) did not undergo diene condensation.



We studied also the Reformatsky reaction with unsaturated cyclic ketones, and after several unsuccessful attempts, we succeeded in bringing about the condensations of 3,5-dimethyl-2-cyclopenten-1-one (XVI) with ethyl bromoacetate and with methyl 2-bromo-2-methylpropionate in presence of mercuric chloride. Under these conditions, the dienic esters (XVII) and (XVIII) were formed immediately:



The resulting dienes gave liquid products with maleic anhydride when heated in benzene to 90°, and hydrolysis of these gave high-melting acids which did not melt sharply but were characterized as their crystalline trimethyl esters. The structures of the dienic esters (XVII) and (XVIII) were proved by ozonization, which gave 2,4-pentanedione and the corresponding malonic acids. Reaction of ethyl bromoacetate with 3,6-dimethyl-2-cyclohexen-1-one* gave a mixture of the normal reaction product and the substance formed by the dehydration of this product. Vacuum distillation of the mixture over potassium hydrogen sulfate gave pure ethyl 2,5-dimethyl-1,5-cyclohexadiene-1-acetate, which also gave a liquid adduct with maleic anhydride.

EXPERIMENTAL

Preparation of 3-Methyl-1,2-butadiene. 2-Methyl-3-buten-2-ol (200 g) was added over a period of 30 minutes to a stirred mixture of 50 g of cuprous chloride, 23 g of ammonium chloride, and 500 ml of concentrated hydrochloric acid, after which stirring was continued further for three hours. The chlorine compounds formed were separated, dried with potassium carbonate, and added with stirring to a hot suspension of 200 g of zinc dust and 60 g of copper powder in 200 ml of butyl alcohol. When the addition was complete, the reaction mixture was refluxed with stirring; stirring was continued while the reaction product was distilled off through a small column. After being dried with calcium chloride and with potassium carbonate, the allene fraction was redistilled through a column. We obtained 95 g of the allene (3-methyl-1,2-butadiene), b.p. 39.2-39.5° (734 mm); n_D^{20} 1.4150.

Dimerization of 3-Methyl-1,2-butadiene. 3-Methyl-1,2-butadiene (70 g) was heated in a metal ampoule at 130° for 48 hours. Fractionation of the reaction products through a product gave: Dimer (IV) (7 g); b.p. 72° (57 mm); n_D^{20} 1.4700; λ_{\max} 243.5 m μ ; ϵ 7.77 · 10³ (heptane); infrared spectrum: 12.7; 11.4; 10.8; 6.9 μ ; Raman spectrum: 1681.1 (very intense); 1645.8 (average intensity); 1479.1; 1380.0; 1283.0 cm⁻¹. Diisopropylidenecyclobutane (III) (18 g); b.p. 99° (80 mm); n_D^{20} 1.5032; λ_{\max} 253.5 m μ ; ϵ 1.02 · 10⁴ (heptane); infrared spectrum: 12.1; 7.4; 6.9 μ ; Raman spectrum: 1676.7 (very intense) 1579; 1443.9; 1380.5; 1257.4; 1145.7; 1086.3;

*The Russian text states that the reactant was methylcyclohexenone, but to obtain the product stated by a Reformatsky reaction followed by dehydration the ketone used must have been that stated here. —Publisher.

1065.0; 630.4; 552.9; 350.4; 147.2 cm^{-1} . Also trimer (38 g), b.p. 145-150° (40 mm), which was not investigated further. The dimers (III) and (IV) did not give crystalline adducts with maleic anhydride in the temperature range 25-100°.

Oxidation of the Dimers (III) and (IV). a) Dimer (III) (3.8 g; b.p. 90°/50 mm) was oxidized with K MnO_4 solution (24 g in 500 ml of water) with stirring and ice cooling. Stirring was continued while excess of permanganate was removed by addition of a little sodium sulfite; 100 ml of aqueous distillate was then distilled off. To 10 ml of the aqueous distillate 25 ml of a solution of 2,4-dinitrophenylhydrazine and phosphoric acid was added. The 1.4 g of dinitrophenylhydrazone isolated was crystallized from alcohol, and this gave 1.2 g (75%) of acetone 2,4-dinitrophenylhydrazone, m.p. 192-193°, undepressed by admixture of a known sample. After removal of acetone the reaction product was filtered from the precipitate of manganese dioxide, which was washed with 100 ml of hot water. The filtrate and wash waters were acidified with the calculated amount of sulfuric acid and vacuum-evaporated to dryness.

The residue was extracted with acetone, and solvent was vacuum-distilled off; crystallization of the new residue from hot water gave 2 g of succinic acid, m.p. 172-173°, undepressed by admixture of a known sample.

Synthesis of the cis-Tetrahydrofuran (VIII). With stirring and ice cooling, a solution of 30 g of diethyl cis-2-cyclohexanedicarboxylate in 200 ml of dry ether was added to a Grignard reagent prepared from 22.5 g of magnesium and 130 g of methyl iodide in 150 ml of dry ether. When the addition of the ester was complete, the mixture was heated under reflux and was then poured into cold dilute sulfuric acid. The reaction product was extracted with 500 ml of ether, the extract was dried with potassium carbonate, the solvent was distilled off. Vacuum distillation of the residue through a column gave 17 g (67%) of the cis-tetrahydrofuran (VIII), b.p. 72-75° (6 mm) and n_D^{25} 1.4683. The literature [13] gives b.p. 80-83° (15 mm) and n_D^{20} 1.4700. From the residue we isolated 2 g of the lactone (IX), m.p. 75-77° (from alcohol). The literature [13] gives m.p. 80°.

Synthesis of the trans-tetrahydrofuran (XII). A solution of 26 g of diethyl trans-1,2-cyclohexanedicarboxylate in 30 ml of ether was added to a Grignard reagent prepared from 12.7 g of magnesium and 76 g of methyl iodide in 75 ml of dry ether. On the next day, the reaction product was decomposed with a mixture of ice and ammonium chloride. Extraction with chloroform gave 18 g of a liquid reaction product, n_D^{20} 1.4835, and this corresponded in analysis to the trans-diol. Found: C 72.56; 72.64; H 12.5; 12.7%. $\text{C}_{12}\text{H}_{24}\text{O}_2$. Calculated: C 72.0; H 12.0%. After vacuum distillation, the trans-diol gave 8.2 g of the trans-tetrahydrofuran (XII), b.p. 110-112° (30 mm) and n_D^{20} 1.4740. Found %: C 79.2; 79.01; H 11.8; 11.92. $\text{C}_{12}\text{H}_{22}\text{O}$. Calculated %: C 79.0; H 12.1.

Tserevitinov estimations showed that both the cis- and the trans-tetrahydrofuran contained only traces (less than 5%) of active hydrogen.

Dehydration of the cis-Tetrahydrofuran (VIII). In the course of eight hours 40 g of the cis-tetrahydrofuran (VIII) was passed in a stream of hydrogen sulfide at 335-350° through a glass tube (diameter 10 mm, length of heated part 25 cm) filled with active alumina. The hydrocarbon part of the catalyzate was washed with water and with 20% potassium hydroxide solution; it was dried with potassium carbonate. Vacuum distillation through a column of 25-plate efficiency gave 10 g of diisopropylidenecyclohexane (VII); b.p. 81.6-81.7° (8 mm); n_D^{21} 1.4912; λ_{max} 259.5 μ ; $\lg \epsilon$ 2.877. Found: C 87.50; 87.37; H 11.80; 11.64%. $\text{C}_{12}\text{H}_{20}$. Calculated: C 87.80; H 12.20%. Diisopropylidenecyclohexane does not give crystalline adducts with maleic anhydride and with benzoquinone in the temperature range 20-120°.

Ozonization of Diisopropylidenecyclohexane (VII). Diisopropylidenecyclohexane (VII) (1.7 g) was ozonized in 59 ml of 95% acetic acid with a stream of ozonized oxygen (0.01 mole/hour) for one hour. One-half of the resulting solution of ozonides was kept at 35° with 5 ml of 30% hydrogen peroxide for 40 hours. The solution was evaporated to dryness, and crystallization from water gave 0.42 g (65%) of adipic acid, m.p. 150-151°, undepressed by admixture of a known sample. The ozonization products in the remainder of the solution were hydrogenated in presence of 0.1 g of platinum dioxide. Catalyst was removed, and distillation gave 10 ml of distillate, in which acetone (28%) was detected and isolated as its 2,4-dinitrophenylhydrazone, m.p. 192-194°. The liquid remaining in the still was evaporated to dryness, and from the residue we isolated 1,2-cyclohexanedione as its dioxime (41%); m.p. 186-188° (from methanol). The literature [23] gives m.p. 189-190°.

Preparation of the Diacetic Ester (X). A mixture of 10 g of the *cis*-tetrahydrofuran (VIII), 10 g of acetic anhydride, and 0.2 g of zinc chloride was heated for three hours at 120°. The reaction product was poured into water and extracted with benzene. The extract was washed with sodium bicarbonate solution and with water and was dried with magnesium sulfate. Benzene was removed under reduced pressure, and we obtained 5.2 g (42%) of the diacetic ester (X), b.p. 145-150° (7 mm) and n_D^{27} 1.4776. Found: C 51.10; 51.20; H 7.95; 8.01%. $C_{12}H_{22}O_4$. Calculated: C 50.70; H 7.74%.

Pyrolysis of the Diacetic Ester (X). The pyrolysis was carried out at 450° in a glass tube filled with Pyrex glass rings; 5 g of the diacetic ester (X) was fed in dropwise. Distillation of the reaction products gave 1 g of diisopropenylcyclohexane, b.p. 70-75° (10 mm) and n_D^{27} 1.4845. Found: C 87.60; 87.50; H 11.95; 12.10%. $C_{12}H_{20}$. Calculated: C 87.80; H 12.20%.

In the ozonolysis of 0.5 g of this diene in acetic acid we isolated formaldehyde as its dimedon derivative (60%), and also adipic acid (30%), m.p. 150-151°.

Reaction of Phenylmagnesium Bromide with *trans*-1,2-Cyclohexanedicarboxylate. A solution of 10 g of the *trans*-ester in 30 ml of dry ether was added over a period of one hour to a Grignard reagent prepared from 6.2 g of magnesium and 26 ml of bromobenzene in 150 ml of ether. The reaction product was left overnight, and on the next day it was decomposed with a mixture of ice and ammonium chloride. This gave 14 g of the *trans*-diol, (XIII), m.p. 170-175°; it contained a small amount of its dehydration products as impurity; it was sparingly soluble in ether. For the *trans*-diol the literature [22] gives m.p. 185°. As the purification of the crude diol is very difficult and results in great losses, for the dehydration we used the crude diol, the content of (XIII) in which was found by analysis to be 92-95%.

Reaction of phenylmagnesium bromide with the *cis*-1,2-cyclohexanedicarboxylic ester gave only the lactone (XIIa), which was obtained in 25% yield; m.p. 175-176° (from ethanol). Found: C 81.86; 81.88; H 7.11; 7.11%. $C_{20}H_{20}O_2$. Calculated: C 82.19; H 6.83%.

Dehydration of the Diol (XIII). A mixture of 1 g of the diol (XIII), 12 ml of acetic acid, and 1.5 ml of concentrated hydrochloric acid was boiled for three hours. When the mixture was cool, the crystals that separated were washed with water and recrystallized from aqueous acetic acid. We obtained 0.5 g of the tetraphenyl diene (XIV); m.p. 247-248°; λ_{max} 234.5 m μ ; ϵ 64200; λ_{max} 296 m μ ; ϵ 11600 (ethanol). Found: C 93.30; 93.13; H 6.78; 6.72%. $C_{32}H_{28}$. Calculated: C 93.4; H 6.8%.

This diene was ozonized in acetic acid, and the ozonide was decomposed by heating it with 30% hydrogen peroxide for 40 hours at 30°. We then isolated benzophenone (75%), m.p. 32° (oxime, m.p. 141-142°), and adipic acid, m.p. 150-152°, undepressed by admixture of known samples. When (XIII) was boiled with a mixture of hydrochloric and acetic acids for 30 minutes, only the unsaturated alcohol (XV), m.p. 112-113°, was isolated. Found: C 89.61; 89.59; H 7.08; 7.21%. $C_{32}H_{30}O$. Calculated: C 89.4; H 7.02%. This alcohol (XV) was converted into the tetraphenyl diene (XIV), m.p. 245-247° and identical with the substance described above, when boiled further with the same mixture.

Ethyl 2,4-Dimethyl-1,4-cyclopentadiene-1-acetate (XVII). To a stirred mixture of 24 g of zinc filings activated with iodine, 60 ml of benzene, and 0.2 g of mercuric chloride we added 5 ml of a solution of 22 g of 3,5-dimethyl-2-cyclopenten-1-one and 42 g of ethyl bromoacetate in 100 ml of benzene. The contents of the flask were heated until a vigorous reaction set in, and with stirring the remainder of the solution was gradually added. Stirring was then continued further for 30 minutes at 80°, and the reaction product was poured into a mixture of ice and 10% sulfuric acid; the extract was carefully washed free from traces of zinc salts and acid, dried with magnesium sulfate, and distilled. We obtained 18 g of ethyl 2,4-dimethyl-1,4-cyclopentadiene-1-acetate (XVII); b.p. 120-125° (16 mm); n_D^{17} 1.4500; λ_{max} 268.5 m μ ; $lg \epsilon$ 4.116 (heptane). Found: C 73.5; 73.4; H 8.25; 8.20%. $C_{11}H_{16}O_2$. Calculated: C 73.8; H 8.89%.

With maleic anhydride in benzene at 100° the ester (XVII) gave a liquid adduct, the hydrolysis of which gave a tricarboxylic acid which did not melt sharply but gave a trimethyl ester of m.p. 92-93° (benzene-petroleum ether mixture). The dienic ester (XVII) (1.8 g) was ozonized in 50 ml of 90% acetic acid at 0° with a stream of ozonized oxygen (0.01 mole/hour) until the double bonds had disappeared, as determined by a test for unsaturation with bromine.

a) To 25 ml of the resulting ozonide solution, 8 ml of 30% hydrogen peroxide was added. The mixture was kept at room temperature for 40 hours, after which acetic acid was vacuum-distilled off with a water bath. The residue was hydrolyzed by heating it in a water bath with 2 ml of 10% aqueous sodium hydroxide, the product was acidified with the calculated amount of sulfuric acid, and the aqueous layer was extracted with ether. We isolated 0.1 g of malonic acid, m.p. 118-121°, undepressed by admixture of a known sample.

b) Platinum dioxide (0.2 g) was added to the remainder of the ozonide solution, and hydrogenation was carried out until hydrogen ceased to be absorbed. A solution of 1 g of 2,4-dinitrophenylhydrazine in 10 ml of acetic acid and 0.5 ml of concentrated hydrochloric acid was added to the solution of reaction products. The solution was heated in a water bath for one hour and filtered, after which acetic acid was vacuum-distilled off. The resulting pyrazolinone (0.2 g) was recrystallized from methanol; m.p. 120-122°. The literature [24] gives m.p. 122°.

Preparation of Methyl $\alpha, \alpha, 2, 4$ -Tetramethyl-1,4-cyclopentadiene-1-1-acetate (XVIII). The Reformatsky reaction was carried out with methyl 2-bromo-2-methylpropionate; the procedure was as in the preceding experiment. However, in this case the reaction was less vigorous, and for its completion it was necessary to apply further heating for two hours in a water bath. After analogous treatment, from 22 g of 3,5-dimethyl-2-cyclopenten-1-one we obtained 16.9 g of the ester (XVIII); b.p. 119-124° (17 mm); n_D^{17} 1.4740; λ_{\max} 264 m μ ; ϵ 1960 (in heptane). Found: C 72.05; 72.05; H 9.32; 9.31%. $C_{12}H_{18}O_2$. Calculated: C 72.22; H 9.44%.

In the ozonolysis, which was carried out as in the preceding experiment, we isolated dimethylmalonic acid (35%) and 2,4-pentanedione in the form of a pyrazolinone, m.p. 120.3°, undepressed by the sample obtained previously. As in the preceding experiment, the adduct of the diene (XVIII) with maleic anhydride was a liquid; after hydrolysis and methylation with diazomethane we obtained a trimethyl ester, m.p. 95°.

The Reformatsky reaction was carried out also with 3,6-dimethyl-2-cyclohexen-1-one*. In this case, however, a mixture of products was formed. Vacuum distillation of these with potassium hydrogen sulfate gave ethyl 2,5-dimethyl-1,5-cyclohexadiene-1-acetate (XXIII); b.p. 126-128° (20 mm); n_D^{20} 1.4985; λ_{\max} 264 m μ ; ϵ 7510 (in heptane). Found: C 73.25; 73.22; H 8.35; 8.47%. Calculated: C 73.8; H 8.89%.

In the ozonolysis of the product by the above-described method, we isolated malonic acid (20%), m.p. 120°, and succinic acid (40%), m.p. 177-178°; in both cases, there was no depression of melting point in mixtures with known samples. The ester (XXIII) again did not give crystalline adducts with maleic anhydride; the trimethyl ester prepared from the liquid adduct had m.p. 85° (from a mixture of benzene and petroleum ether).

SUMMARY

1. A detailed study was made of the Grignard reaction with esters of cis- and trans-1,2-cyclohexanedicarboxylic acids.
2. 1,2-Bis(diphenylmethylene cyclohexane and diisopropylidenecyclohexane, and also their cyclobutane analogs, do not undergo diene condensation with maleic anhydride and with benzoquinone.
3. The Reformatsky reaction with 3,5-dimethyl-2-cyclopenten-1-one leads to 2,4-dimethyl-1,4-cyclopentadiene-1-acetic acids.

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*Original Russian pagination. See C. B. translation.

SYNTHESIS OF 5'-BENZOYL-2'-HYDROXYCHALCONES AND RELATED FLAVONOID COMPOUNDS

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Among the various derivatives of 3-phenylacrylophenones (chalcones), 2'-hydroxychalcones present special interest because they are close in structure to many coloring matters met in nature, which are polyhydroxy- and polymethoxy-chalcones and related flavanones and flavonols (hydroxyflavones). Various derivatives of 2'-hydroxychalcones have been the subject of particularly extensive investigations. The interest in the investigation of these compounds has been intensified by the fact that they show some bacteriostatic action. In the present paper, we describe the synthesis of 5'-benzoyl-2'-hydroxychalcones and related flavonoid compounds, which forms a part of the investigational program of our laboratory in the field of 2'-hydroxychalcones and related heterocyclic compounds [1].

5'-Benzoyl-2'-hydroxyacetophenone [2] was condensed with aldehydes in ethanol in presence of some 40% potassium hydroxide solution. In all cases, we obtained derivatives of 5'-benzoyl-2'-hydroxychalcone (I), for a) with concentrated sulfuric acid, the products gave a characteristic dark-red color and with an alcoholic solution of ferrous chloride, a yellow to reddish-brown color; b) they dissolved, though only moderately, in dilute sodium hydroxide solution, giving a yellow to orange color; they gave Wilson's test with boric and citric acids [3]; and c) they formed benzoic esters, which confirmed the presence of a free hydroxy group.

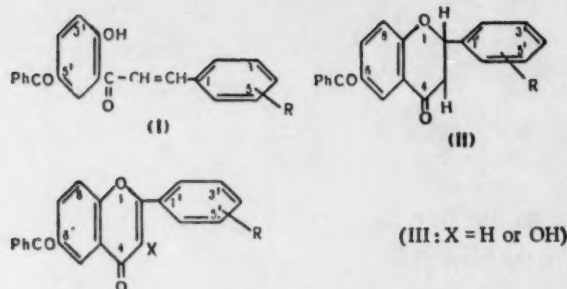
The use of a 20% or 60% potassium hydroxide solution in the condensation process lowered the yields. The chalcones obtained were isomerized by boiling them with dilute alcoholic solutions of acids [4] to 6-benzoylflavanones (II). Simultaneous cyclization and dehydrogenation of 5'-benzoyl-2'-hydroxychalcones with the aid of a solution of selenium dioxide in isopentyl alcohol [5] gave 6-benzoylflavones (III, X = H), and after cyclohydroxylation by means of cold alkaline, hydrogen peroxide [6], we obtained the corresponding 6-benzoyl-3-hydroxyflavones (6-benzoylflavonols) (III, X = OH).

Hence, the presence of a 5'-benzoyl group in 2'-hydroxyacetophenone does not hinder the formation of chalcones and related flavonoid compounds. This conclusion is confirmed by analogous observations on other substituted 2'-hydroxychalcones and many of their derivatives [7].

EXPERIMENTAL

5'-Benzoyl-2'-hydroxychalcones (I), 6-benzoylflavanones (II), 6-benzoylflavones (III, X = H), and 6-benzoyl-3-hydroxyflavones (III, X = OH) were prepared by general methods, which are described below. The compounds obtained are listed in Tables 1-4. All melting points are uncorrected.

5'-Benzoyl-2'-hydroxychalcones (I). A solution of 1 g of 5'-benzoyl-2-hydroxyacetophenone and 0.6-0.7 g of the aldehyde in 20 ml of ethanol was added with shaking to 20 ml of 40% potassium hydroxide solution. The mixture was heated for about five minutes in a water bath and left for the optimum time or overnight at room temperature (25-30°); the reaction mixture became considerably darker and redder in color. Acidified ice water



was added, and a colored solid separated; it was collected, washed with a solution of sodium bicarbonate, and crystallized (yield 0.8-1.2 g). In the case of the chalcones (3), (5), (7), and (11), the mixture was kept for more than 160 hours at room temperature.

TABLE 1. 5'-Benzoyl-2'-hydroxychalcones

No.	Substituent R	Color and form of crystals	M.p. (°C)	Formula	Calculated (%)		Found (%)	
					C	H	C	H
1	—	Yellow needles (E)	114	C ₂₂ H ₁₄ O ₃	80,48	4,87	80,21	4,62
2	Benzoate of (1)	Short yellowish needles (A)	134	C ₂₉ H ₂₀ O ₄	80,56	4,62	80,26	4,41
3	2-Hydroxy	Yellowish needles (E)	159	C ₂₂ H ₁₆ O ₄	76,74	4,65	76,53	4,41
4	Benzoate of (3)	Brown grains (A)	235	C ₃₆ H ₂₄ O ₆	78,27	4,34	78,01	4,09
5	3-Hydroxy	Short yellow needles (C + P)	153	C ₂₂ H ₁₆ O ₄	76,74	4,65	76,48	4,42
6	Benzoate of (5)	Pale yellow thin plates (E)	109	C ₃₆ H ₂₄ O ₆	78,27	4,34	78,06	4,11
7	4-Hydroxy	Yellow needles (A)	194	C ₂₂ H ₁₆ O ₄	76,74	4,65	76,54	4,36
8	Benzoate of (7)	Brownish grains (E)	240	C ₃₆ H ₂₄ O ₆	78,27	4,34	78,02	4,07
9	4-Methoxy	Gleaming orange needles (E)	124	C ₂₃ H ₁₈ O ₄	77,09	5,02	76,81	4,83
10	Benzoate of (9)	Clusters of yellow needles (E)	96	C ₃₀ H ₂₀ O ₅	77,93	4,32	77,59	4,08
11	4-Hydroxy-3-methoxy	Orange plates (E)	138	C ₂₃ H ₁₈ O ₅	73,79	4,81	73,48	4,53
12	Benzoate of (11)	Gleaming pale-yellow needles	109	C ₃₇ H ₂₆ O ₇	76,30	4,46	76,06	4,29
13	3,4 Dimethoxy	Gleaming yellow needles (A)	185	C ₂₄ H ₂₀ O ₅	74,23	5,15	74,01	5,36
14	Benzoate of (13)	Fine yellowish needles (A)	137	C ₃₁ H ₂₄ O ₆	75,60	4,87	75,32	4,58
15	3,4-Methylenedioxy	Orange needles (E)	173	C ₂₃ H ₁₆ O ₅	74,20	4,30	74,00	4,03
16	Benzoate of (15)	Fine needles (A)	142	C ₃₀ H ₂₀ O ₆	75,63	4,20	75,38	3,88
17	3-Nitro	Yellow needles (A)	182	C ₂₂ H ₁₅ O ₅ N	70,78	4,02	70,50	3,77
18	Benzoate of (17)	Brownish grains (E)	139	C ₂₉ H ₁₉ O ₆ N	72,97	3,98	72,75	3,73
19	3-Chloro-4-methoxy	Yellow needles (A)	178	C ₂₃ H ₁₇ O ₄ Cl	Cl 9,4		Cl 8,82	
20	Benzoate of (19)	Fine yellowish needles (A)	124	C ₃₀ H ₂₁ O ₆ Cl	Cl 7,15		Cl 6,83	

Notes. (A) —50% acetic acid; (B) —benzene; (C) —chloroform; (E) —ethanol; (P) —petroleum ether, b.p. 60-80°. These symbols are used throughout the tables.

TABLE 2. 6-Benzoylflavonones (II)

No.	Substituent R	Color and form of crystals	M.p. (°C)	Formula	Calculated (%)		Found (%)	
					C	H	C	H
21	—	Fine yellowish needles (A)	187	C ₂₂ H ₁₆ O ₃	80,48	4,88	80,24	4,62
22	2-Hydroxy	Yellow grains (E)	95	C ₂₂ H ₁₆ O ₄	76,74	4,65	76,42	4,41
23	3-Hydroxy	Yellow grains (E)	175	C ₂₂ H ₁₆ O ₄	76,74	4,65	75,54	4,65
24	4-Hydroxy	Fine yellowish needles (A)	182	C ₂₂ H ₁₆ O ₄	76,74	4,65	76,48	4,38
25	4-Methoxy	Gleaming yellow needles (E)	141	C ₂₃ H ₁₈ O ₄	77,09	5,02	76,87	4,72
26	4-Hydroxy-3-methoxy	Yellow grains (E)	172	C ₂₃ H ₁₈ O ₅	73,79	4,81	73,48	4,54
27	3,4-Dimethoxy	Orange needles (E)	174	C ₂₄ H ₂₀ O ₅	74,23	5,15	73,95	4,82
28	3,4-Methylenedioxy	Pale-yellow plates (E)	156	C ₂₃ H ₁₆ O ₅	74,20	4,30	73,96	4,03
29	3-Nitro	Fine yellow needles (A)	140	C ₂₂ H ₁₅ O ₅ N	70,78	4,02	70,50	3,79
30	3-Chloro-4-methoxy	3,4-Methylenedioxy	152	C ₂₃ H ₁₇ O ₄ Cl	Cl=9,04		Cl=8,79	

TABLE 3. 6-Benzoylflavones (III, X = H)

No.	Substituent R	Color and form of crystals	M.p. (°C)	Formula	Calculated (%)		Found (%)	
					C	H	C	H
31	—	Colorless grains (P)	164	C ₂₂ H ₁₄ O ₃	80,98	4,29	80,75	4,04
32	2-Hydroxy	Brownish grains (E)	218	C ₂₂ H ₁₄ O ₄	77,20	4,09	77,01	3,76
33	3-Hydroxy	Pale-yellow grains (A)	138	C ₂₂ H ₁₄ O ₄	77,20	4,09	76,95	3,87
34	4-Hydroxy	Brown grains (A)	298	C ₂₂ H ₁₄ O ₄	77,20	4,09	76,92	3,77
35	4-Methoxy	Fine yellow needles (B)	206	C ₂₃ H ₁₆ O ₄	77,54	4,49	77,28	4,20
36	4-Hydroxy-3-methoxy	Yellowish grains (E)	191	C ₂₃ H ₁₆ O ₅	74,20	4,30	73,97	4,04
37	3-4-Dimethoxy	Yellowish grains (E)	202	C ₂₄ H ₁₈ O ₅	74,51	4,66	74,24	4,44
38	3,4-Methylenedioxy	Fine yellowish needles (C + P)	211	C ₂₃ H ₁₄ O ₅	74,59	3,78	74,34	3,52
39	3-Nitro	Yellowish grains (P)	206	C ₂₂ H ₁₃ O ₅ N	71,15	3,50	70,85	3,26
40	3-Chloro-4-methoxy	Yellow grains (E)	211	C ₂₃ H ₁₅ O ₄ Cl	Cl=9,09		Cl=8,82	

The benzoic esters of the chalcones were prepared by heating a mixture of the substance, benzoyl chloride, and a few drops of pyridine. When the reaction mixture was diluted with acidified water, a solid separated and was recrystallized.

TABLE 4. 6-Benzoyl-3-hydroxyflavones (III, X = OH)

No.	Substituent R	Color and form of crystals	M.p. (°C)	Formula	Calculated (%)		Found (%)	
					C	H	C	H
41	—	Fine yellowish needles (E)	227	C ₂₂ H ₁₄ O ₄	77,20	4,09	77,09	3,78
42	Acetate of (41)	Thin pale-yellow plates (E)	157	C ₂₄ H ₁₆ O ₅	75,01	4,16	74,80	4,01
43	2-Hydroxy	Thin pale-yellow plates (E)	235	C ₂₂ H ₁₄ O ₅	73,74	3,91	73,53	3,62
44	Acetate of (43)	Yellowish grains (E)	90	C ₂₄ H ₁₆ O ₆	71,99	3,99	71,74	3,74
45	3-Hydroxy	Fine yellowish needles (E)	259	C ₂₂ H ₁₄ O ₅	73,74	3,91	73,52	3,58
46	Acetate of (45)	Colorless grains (E)	104	C ₂₄ H ₁₆ O ₆	71,99	3,99	71,76	3,76
47	4-Hydroxy	Pale-yellow needles (E)	210	C ₂₂ H ₁₄ O ₅	73,74	3,91	73,51	3,67
48	Acetate of (47)	Gleaming yellowish needles (E)	137	C ₂₄ H ₁₆ O ₆	71,99	3,99	71,72	3,68
49	4-Methoxy	Fine yellowish needles (E)	240	C ₂₃ H ₁₆ O ₅	74,20	4,30	73,95	4,03
50	Acetate of (49)	Gleaming yellowish needles (E)	185	C ₂₅ H ₁₈ O ₆	72,46	4,34	72,26	4,07
51	4-Hydroxy-3-methoxy	Gleaming yellowish needles (E)	163	C ₂₃ H ₁₆ O ₆	71,14	4,12	70,82	3,89
52	Acetate of (51)	Clusters of pale-yellow needles	87	C ₂₅ H ₁₈ O ₇	69,76	4,18	69,42	3,92
53	3,4-Dimethoxy	Fine yellowish needles (A)	208	C ₂₄ H ₁₈ O ₆	71,64	4,47	71,44	4,23
54	Acetate of (53)	Pale-yellow grains (A)	140	C ₂₆ H ₂₀ O ₇	70,28	4,50	70,06	4,18
55	3,4-Methylenedioxy	Fine yellowish needles (A)	234	C ₂₈ H ₁₄ O ₆	71,50	3,62	71,22	3,38
56	Acetate of (55)	Colorless needles (E)	205	C ₂₅ H ₁₆ O ₇	70,09	3,73	69,88	3,43
57	3-Nitro	Fine yellowish needles (A)	296	C ₂₂ H ₁₃ O ₆ N	68,22	3,35	68,02	3,07
58	Acetate of (57)	Brown grains (A)	156	C ₂₄ H ₁₅ O ₇ N	67,13	3,49	66,81	3,23
59	3-Chloro-4-methoxy	Fine yellowish needles (A)	247	C ₂₃ H ₁₅ O ₅ Cl	Cl=8,73		Cl=8,49	
60	Acetate of (59)	Colorless needles (E)	169	C ₂₅ H ₁₇ O ₆ Cl	Cl=7,91		Cl=7,63	

The Flavanone (II, R = H). A 10% solution of sulfuric acid was gradually added to a solution of 0.3 g of 5'-benzoyl-2'-hydroxychalcone in 20 ml of ethanol until a slight turbidity formed (20 ml of acid was required). The turbidity disappeared when about 25 ml or more ethanol was added, and the clear solution was refluxed in a water bath for 30-35 hours. The ethanol was removed, and the residual liquid yielded a pale yellow precipitate when cooled; the precipitate was recrystallized (yield 0.2 g). With concentrated sulfuric acid this precipitate gave a reddish color, whereas no coloration occurred when alcoholic ferrous chloride was added.

The Flavone (III, R = H, X = H). A mixture of 0.3 g of 5'-benzoyl-2'-hydroxychalcone and 0.3 g of selenium dioxide in dry isopentyl alcohol (15-20 ml) was refluxed in an oil bath at 150-160° for 12-14 hours. The reaction mixture was filtered hot to remove precipitated selenium, and the filtrate was steam-distilled to remove isopentyl alcohol. The residual liquid was cooled and gave a brown paste of a solid; this was crystallized from solvent (yield 0.2 g). With concentrated sulfuric acid it gave a greenish fluorescence, and there was no color reaction with ferrous chloride.

The Hydroxyflavone (III, R = H, X = OH). To a solution of 0.3 g of 5'-benzoyl-2'-hydroxychalcone in 20 ml of ethanol we added 20 ml of a 5% solution of sodium hydroxide. The homogeneous mixture was cooled in an ice bath, and 4-5 ml of 17% hydrogen peroxide was added. The mixture was kept in the ice bath for about

three hours. The dark red solution gradually became yellow, and a yellow solid began to separate. The reaction mixture was then kept at room temperature (25-30°) for 20-24 hours. At the end of this time the mixture was slowly poured into ice water containing hydrochloric acid. The solid that separated was filtered off, washed with water, and recrystallized (yield 0.2 g). The hydroxyflavone dissolved in excess of dilute sodium hydroxide solution, and with concentrated sulfuric acid it gave a greenish-blue fluorescence.

The acetic ester, which was prepared by the action of acetic anhydride in pyridine, was crystallized in the same way.

SUMMARY

5'-Benzoyl-2'-hydroxychalcones were synthesized by the condensation of 5'-benzoyl-2'-hydroxyacetophenone with aromatic aldehydes in presence of an ethanolic solution of potassium hydroxide. Derivatives of 6-benzoylflavonoids were prepared from chalcones.

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SYNTHESIS, PROPERTIES, AND RAMAN SPECTRA OF
1,4,4a,5,8,8a-HEXAHYDRO-1,4:5,8-DIMETHANONAPHTHALENE
AND DECAHYDRO-1,4:5,8-DIMETHANONAPHTHALENE

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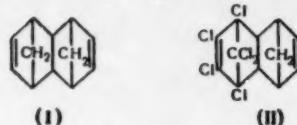
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February, 1960

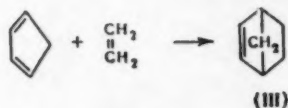
Original article submitted June 20, 1958

The tetracyclic hydrocarbon 1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene (I) may be regarded as a derivative of partially hydrogenated naphthalene in which each six-membered ring has the "boat" shape,



rigidly fixed by means of the methylene bridge. The molecule of such a hydrocarbon is compact and has a definite Bayer strain. Its properties and spectrum characteristics may therefore be of definite interest; all the more so, in that the very successful insecticides aldrin (II) and its stereoisomer isodrin have an analogous carbon skeleton and may be regarded as polyhalogen derivatives of this hydrocarbon. However, the hydrocarbon (I) has not been described in the chemical literature, though it is mentioned in one patent [1]. The present investigation was devoted to the synthesis of this hydrocarbon and a study of its properties.

As is well known, the preparation of hydrocarbons with the carbon skeleton of norbornane (bicyclo[2,2,1]heptane) has become quite accessible as a result of the development of diene syntheses based on cyclopentadiene. By way of example, the condensation of cyclopentadiene with ethylene gives 2-norbornene (III) [2]; the condensations of cyclopentadiene with propene, butenes, 1-heptene, and 1-octene give various 5-alkyl-2-norbornenes [3-5]. We studied the condensation of cyclopentadiene with acetylene* and showed [8] that reaction occurs by



the diene-synthesis scheme and gives 2,5-norbornadiene (IV). A closer investigation of the reaction products showed that, in the course of the reaction, (IV) undergoes further condensation with cyclopentadiene and forms the by-product 1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene (I), which may be obtained in the rectification of the residue after the separation of (IV):

* This reaction is described also in the patent literature [6, 7].

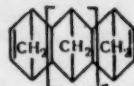


In the condensation of cyclopentadiene with acetylene in a flow apparatus, the yield of (I) varies in the range 5.5-8.5%. In Table 1, we give the yields of (IV) and (I) (percent on cyclopentadiene taken) for different reaction conditions.

TABLE 1. Yields of 2,5-Norbornadiene (IV) and Hexahydrodimethanonaphthalene (I) in the Condensation of Cyclopentadiene with Acetylene

Temperature (°C)	341	341	341	360
Pressure of C ₂ H ₂ (atm)	20	20	20	10
Ratio C ₅ H ₆ : C ₂ H ₂	1 : 2	1 : 2	1 : 2	1, 2
Space velocity (liters of C ₅ H ₆ /liter · hour)	0,07	0,11	0,23	0,20
Yield of norbornadiene (%)	54,5	48,4	45,4	21,7
Yield of hexahydrodimethanonaphthalene (%)	5,4	7,6	8,4	7,0

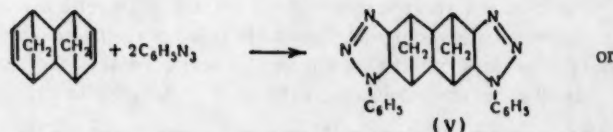
Hexahydrodimethanonaphthalene was prepared by us also by the condensation of norbornadiene with cyclopentadiene in an autoclave at elevated temperature. At 175° with a heating time of 4.5 hours (I) was formed in 21.5% yield, calculated on the cyclopentadiene taken, or 41% yield, calculated on the amount of norbornadiene that reacted. The reaction must be carried out with a small excess of norbornadiene; otherwise, the hexahydrodimethanonaphthalene formed undergoes further condensation with cyclopentadiene and there is an increase in the amount of higher-boiling fractions, which probably have the structure:



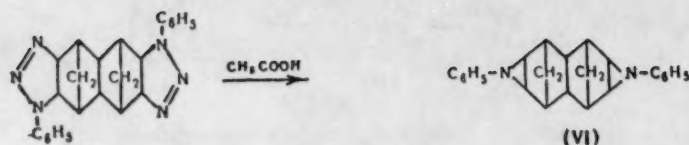
in which $n = 1, 2, \dots$

Hexahydrodimethanonaphthalene (I) is a colorless liquid, m.p. 1°; it has good thermal stability and distills without decomposition at atmospheric pressure (217°). Though (I) has the same carbon skeleton as aldrin and isodrin (II), the absence of chlorine atoms results in an absence of insecticidal properties*.

A double bond in the norbornane system is readily identified by the preparation of the adduct with phenyl azide [9]. Hexahydrodimethanonaphthalene reacts vigorously with phenyl azide, and addition occurs at both double bonds:



* Toxicological investigations were carried out by E. F. Granin at the Fertilizer and Insectifungicide Research Institute.

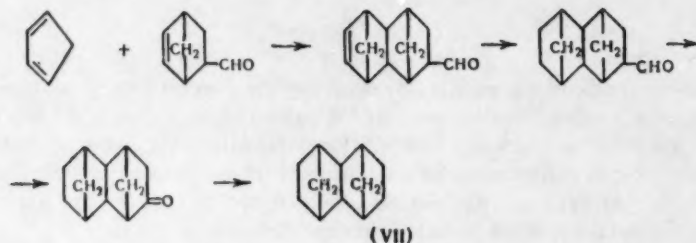


The resulting adduct (V) is a bis-1,2,3-triazoline, and like other triazolines of the norbornane series [10], under the action of acetic acid or other acid agents, it readily loses two nitrogen atoms from each triazoline ring with formation of the corresponding bisethylenimine (VI).

Hydrogenation of the hexahydrodimethanonaphthalene gave decahydro-1,4:5,8-dimethanonaphthalene (VII), a hydrocarbon of m.p. 36.0-36.5° with a pleasant camphorlike odor:



In its properties, (VII) was found to be identical with the decahydrodimethanonaphthalene which Alder and co-workers earlier [11] prepared as follows:



The hexahydrodimethanonaphthalene and decahydrodimethanonaphthalene can theoretically exist in three stereoisomeric forms: exo-exo, exo-endo, and endo-endo. However, the hydrocarbons (I) and (VII) which we prepared and the decahydrodimethanonaphthalene synthesized by Alder had the same configuration and were probably sterically homogeneous; however, the actual configuration of these hydrocarbons is at present unknown.

It is very notable that in the Raman spectra of the hydrocarbons (I) and (VII) most of the lines are unusually sharp and intense; diffuse lines are almost absent. This situation probably arises from the rigidity of the configurations of the molecules. The considerable resemblances between the spectra of hexahydrodimethanonaphthalene (I) and 2-norbornene (III) (Table 2) and between those of decahydrodimethanonaphthalene (VII) and norbornane (Table 3) [12], particularly in the region of 800 cm^{-1} , are very striking. The frequencies of lines of norbornene and norbornane given in the table are characteristic also for some of their alkyl derivatives; also, some of the lines of the former occur also in the spectrum of cyclopentene [13]. It may be stated, therefore, that in the spectrum of such a relatively complex molecule as (I), the presence of the simpler structural element, the five-membered ring, manifests itself. This fact, and also the fact that the spectra of bicyclic hydrocarbons intermediate in complexity between (I) and cyclopentene homologs are similar to those of the hydrocarbons studied, is worthy of attention, because the spectra of condensed systems are not usually very similar to those of the separate ring systems (cf., e.g., benzene with naphthalene or cyclohexane with decahydronaphthalene).

The lines of the hexahydrodimethanonaphthalene (I) spectrum corresponding to the valence vibration of the double bond lie in the region of 1570 cm^{-1} , i.e., in the same place as the corresponding lines of norbornene and some of its homologs [12]. However, in the spectrum under consideration, this line is a doublet (1564 and 1570 cm^{-1}) with components of almost equal intensity. It is difficult to say whether the presence of two lines is the result of the splitting of the frequencies of associated vibrations of two C=C bonds, or whether these lines belong to different (two or more) conformations of the molecule of the compound under investigation.

TABLE 2. Comparison of the Characteristic Lines of the Raman Spectra of Hexahydrodimethanonaphthalene and 2-Norbornene

Hexahydrodimethanonaphthalene (I)		2-Norbornene (II) [12]	
Frequency $\Delta\nu(\text{cm}^{-1})$	Intensity I	Frequency $\Delta\nu(\text{cm}^{-1})$	Intensity I
425	(250)	{ 385 (18)* 477 (54) 903 (70)*	
892	(43)		
903	(70)		
926	(140)	938 (100)	
960	(135)	965 (68)*	
1092	(150)	1091 (76)*	
1109	(76)	1114 (46)	
1130	(130)	1126 (80)	
1298	(14)	1297 (13)*	

*Lines of the cyclopentenespectrum [13].

TABLE 3. Comparison of the Characteristic Lines of the Raman Spectra of Decahydrodimethanonaphthalene and Norbornane

Decahydrodimethanonaphthalene (VII)		Norbornane [12]	
Frequency $\Delta\nu(\text{cm}^{-1})$	Intensity I	Frequency $\Delta\nu(\text{cm}^{-1})$	Intensity I
873	(74)	872 (140)	
918	(250)	922 (130)	
1107	(82)	1117 (30)	
		1126 (90)	
1133	(56)	1139 (20)	

Calculated MR 47.88. Found: M (determined cryoscopically in benzene) 157.5; 157.2. $\text{C}_{12}\text{H}_{14}$. Calculated: M 158.2. Found: C 91.00; 91.23; H 9.09; 8.89%. Calculated: C 91.10; H 8.90%.

Reaction of Hexahydrodimethanonaphthalene (I) with Phenyl Azide. Phenyl azide was prepared by the action of sodium nitrite on phenylhydrazine in presence of hydrochloric acid [14]. A mixture of 0.8 g of hexahydrodimethanonaphthalene and 1.8 g of phenyl azide was prepared. After 5-10 minutes there was a spontaneous rise in temperature, and crystallization then occurred. The resulting bistriazoline (V) was purified by boiling it with acetone (twice), for it is insoluble in ether, alcohol, acetone, ethyl acetate, and chloroform. Yield 1.4 g (70%); m.p. 227-228° (decomp.). Found: C 72.17; 72.33; H 6.02; 6.01; N 22.08; 22.27%. $\text{C}_{24}\text{H}_{24}\text{N}_6$. Calculated: C 72.71; H 6.09; N 21.20%.

When an attempt was made to recrystallize this bistriazoline from acetonitrile, four atoms of nitrogen were eliminated with formation of the bisethylenimine (VI). The latter is obtained also by the treatment of the bistriazoline with acetic acid. The bisethylenimine crystallized well from ethyl acetate; m.p. 223-224°. Found: 84.22; 84.35; H 7.09, 7.09; N 8.70; 8.71%. $\text{C}_{24}\text{H}_{24}\text{N}_2$. Calculated: C 84.68; H 7.09; N 8.23%.

EXPERIMENTAL

Condensation of 2,5-Norbornadiene (IV) with Cyclopentadiene. A 250-ml autoclave was loaded with 13.3 g (0.144 mole) of 2,5-norbornadiene (IV) and 7.4 g (0.112 mole) of freshly distilled cyclopentadiene, and the autoclave was heated at 175° for 4.5 hours. The products unloaded amounted to 19.8 g and were separated into the following fractions by distillation:

Fraction	B.p. in °C (p in mm)	Weight (g)	n_D^{20}
I	Do 86/752	1.3	1.4521
II	86-93/752	5.5	1.4720
III	66-80(10)	1.8	1.5188
IV	80-85(10)	3.8	1.5321
V	85-107(10)	0.2	1.5408
Residue		4.4	

Fraction II was unchanged (IV). Fraction III was cyclopentadiene dimer. Fraction IV was hexahydrodimethanonaphthalene (I), the yield of which on the amount of cyclopentadiene taken for reaction was 21.5%. On the amount of (IV) that reacted, the yield of (I) was 41%. For the isolation of (I) in a purer state, the product from several experiments was combined and vacuum-distilled through a column of 80-plate efficiency. For fractionation we took 81.3 g of hydrocarbon of n_D^{20} 1.5309. The results of the fractionation are given in Table 4 and Fig. 1. In Fig. 1, the abscissae are fractions of distillate driven off (% by weight), and the ordinates are refractive indices for Curve 1, densities for Curve 2, and freezing points for Curve 3. The boiling point curve is not given because small variations of pressure during vacuum-fractionation through a column caused variations of boiling point and this makes the boiling point curve not characteristic.

The hexahydrodimethanonaphthalene obtained after distillation through the column (Fractions II-VIII) had the following properties: b.p. 74.8° (6 mm), 217° (760 mm); f.p. +1°; n_D^{20} 1.5322; d_4^{20} 1.0374. Found: MR 47.33. $\text{C}_{12}\text{H}_{14}$. 2f

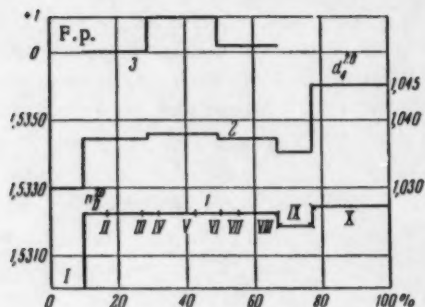


Fig. 1. Constants of Hexahydrodimethanonaphthalene Fractions

1,4,4a,5,8,8a-Hexahydro-1,4:5,8-dimethanonaphthalene, $\Delta\nu$: 136(12), 195(4), 234(26), 287(2), 310(96), 338(3), 385(2), 425(220), 503(22), 554(46), 640(13), 682(70), 709(7), 737(14), 759(17), 798(47), 807(15), 825(5), 844(16), 892(43), 903(70), 926(140, sh), 960(135), 992(36), 1017(41), 1051(36), 1092(150, sh), 1109(76, sh), 1130(130, sh), 1171(1), 1203(31, sh), 1214(50), 1248(34), 1269(4), 1298(14), 1320(5), 1353(9), 1380(3b), 1444(5, bg), 1459(38), 1481(3, b), 1540(4, b), 1564(130), 1570(130), 2865(70, sh), 2886(30), 2905(80), 2915(100, b), 2935(170), 2966(540, b), 3038(50), 3060(360), 3137(40).

Decahydro-1,4:5,8-dimethanonaphthalene, $\Delta\nu$: 171(4), 232(17), 327(72), 381(4, b), 417(39, b), 479(3), 501(10), 555(35), 581(1), 645(1), 722(66), 742(1), 787(23), 817(46), 838(12), 873(74, db), 918(250), 933(29), 946(33), 956(10), 986(96), 1025(27), 1036(48), 1056(64), 1107(82), 1133(56), 1141(29), 1175(48), 1192(33), 1211(18), 1225(29), 1248(2), 1268(15), 1284(20), 1301(13), 1327(8), 1347(18), 1375(2), 1449(54), 1458(58), 1474(3), 1493(17, b), 2870(190), 2886(150), 2910(100), 2930(300), 2948(600), 2963(500), 2992(50).

TABLE 4. Results of the Fractionation of Hexahydrodimethanonaphthalene

Fraction	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	F.p. (°C)	Amount (g)
I	68,5—70,7(5)	1,5299	1,0298	<-40	7,0
II	From 70.7°/5 to 74.8°/6	1,5322	1,0369	-0,5—+0,5	4,5
III		1,5322	1,0368		9,1
IV		1,5322	1,0374	+1,0	2,1
V		1,5322			7,1
VI		1,5322			4,9
VII		1,5322	1,0371	0+0,2	3,5
VIII		1,5322	1,0369		7,1
IX		1,5318	1,0352		7,2
X*		1,5324	1,0455		16,2
Residue		Tar			7,9
Losses					4,7

*Fraction X was obtained at the expense of considerable overheating of the filling of the column with the object of a more complete removal of distillate substance from the flask.

Hydrogenation of Hexahydrodimethanonaphthalene (I).

The hydrocarbon of m.p. 0-2° (10.0 g) was hydrogenated in cyclohexane (30 ml) solution in the cold in presence of 0.7 g of platinum deposited on charcoal. The amount of hydrogen absorbed was 2.8 liters (760 mm, 20°), and theory requires the absorption of 2.83 liters (760 mm, 20°). The solvent was distilled off, and the hydrogenation product was then distilled from a flask. We obtained 8.8 g of a fraction of b.p. 114.0-114.5° (20 mm); m.p. 36.0-36.5° (from ethanol). Found: C 88.86; 88.87; H 11.08; 11.07% $C_{12}H_{12}$. Calculated: C 88.84, H 11.16%. The literature [11] gives m.p. 36-37°.

Raman Spectra. These were studied by the method described in [15]. In the parentheses following the values of frequency, we give the intensity on a scale on which the intensity of the maximum of the cyclohexane line at $\Delta\nu = 802\text{ cm}^{-1}$ is 250. The other symbols characterize the lines as follows: b—broad; sh—sharp; bg—the line stands on a background of considerable intensity; db—doublet.

SUMMARY

1. 1,4,4a,5,8,8a-Hexahydro-1,4:5,8-dimethanonaphthalene was synthesized by the diene condensation of cyclopentadiene with 2,5-norbornadiene; the same hydrocarbon was isolated as a by-product in the preparation of 2,5-norbornadiene by the condensation of cyclopentadiene with acetylene. Derivatives of this hydrocarbon were prepared: the corresponding bistriazoline and bisethylenimine.

2. Decahydro-1,4:5,8-dimethanonaphthalene was prepared by the hydrogenation of the hexahydrodi-methanonaphthalene.

3. The Raman spectra of the hydrocarbons obtained were studied, and it was shown that there is a considerable resemblance between these spectra and those of 2-norbornene and norbornane, respectively.

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SEPARATION OF THE HIGH-MOLECULAR-WEIGHT HYDROCARBONS OF PETROLEUM BY A COMBINATION OF THE METHODS OF MOLECULAR DISTILLATION AND CHROMATOGRAPHY

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Methods of separating mixtures of organic compounds of high molecular weight are acquiring more and more scientific and practical importance. The more complex the mixture, the more difficult the task of separating it. The task is not usually the isolation of individual compounds from the mixture, but the resolution of the mixture into groups of compounds which are close in chemical structure and do not differ greatly in molecular weight. Without such simplification of the composition of a complex mixture of organic compounds of high molecular weight, it is difficult to make an approach to the solution of the question of their chemical structures. The preliminary separation of such mixtures into relatively homogeneous groups of substances is now becoming of great importance and is often the determining stage in the preparation of such raw material for chemical processing.

The separation of such mixtures is based on two principles: a) utilization of the marked differences in molecular structure between the substances present in the multicomponent system to be separated, or, as this principle is usually defined, separation according to types of molecule; b) separation of complex mixtures of compounds of high molecular weight into fractions in accordance with the dimensions of their molecules.

The first group of methods of separation includes chromatography, thermodiffusion, and the selective action of solvents. Efficient separation of mixtures by these methods is attained more readily and successfully, the greater the differences in chemical structure between the components of the mixture; this assumes relatively little variation in molecular weight. Methods of the second group, such as centrifugation, molecular distillation, and fractional precipitation, are used for the separation of the components of mixtures of compounds of high molecular weight in accordance with the sizes or weights of the molecules. The effectiveness of such methods is the greater, the greater the difference in the molecular weights of the components of the mixture to be separated.

In the case of the high-molecular-weight compounds of petroleum, we are concerned with multicomponent mixtures in which the components differ both in type of chemical structure and in molecular size, though differences of both these kinds are masked by the presence of a considerable proportion of compounds of intermediate types. In such a case, we can expect to be appreciably successful only if we combine the two types of methods of separation, i.e., methods of separation according to type of molecule alternating with methods of separation according to molecular size. Not only the methods selected for a separation, but also the order in which they are applied, will vary according to the complexity and variety of the components. Thus, a fully hydrogenated petroleum oil is more effectively separated by chromatography than by the method of thermodiffusion [1], whereas for the separation of sulfur compounds present in petroleum from the hydrocarbon part a combination of chromatography and thermodiffusion is found to be effective [2].

In our investigations we have successfully used chromatography on silica gel for the separation of the resinous part of a petroleum from the hydrocarbons of high molecular weight, and also for the further separation both of the resins and of the hydrocarbons into groups of substances that are closer together in composition and structure [3]. In the present investigation we used a combination of chromatography and molecular distillation for the separation of the high-molecular-weight part of petroleum into fractions which were as homogeneous as possible.

EXPERIMENTAL

As material for investigation, we took the high-molecular-weight part of Romashkin petroleum, b.p. above 325°, after it had been freed from the resin-asphaltene part. To avoid the thermal decomposition of the higher-molecular-weight components of petroleum during the distillation of the light part, b.p. below 325°, the distillation was carried out under reduced pressure, which rendered it unnecessary to heat the petroleum above 215°. The temperature of the liquid in the still of the molecular-distillation apparatus also did not exceed 215°. Figure 1 gives the general scheme for the separation of the high-molecular-weight part from the petroleum (upper part of the scheme, demarcated by the horizontal broken line) and the scheme for its separation into narrow fractions of greater chemical homogeneity by successive applications of methods of molecular distillation and chromatography (lower part of scheme).

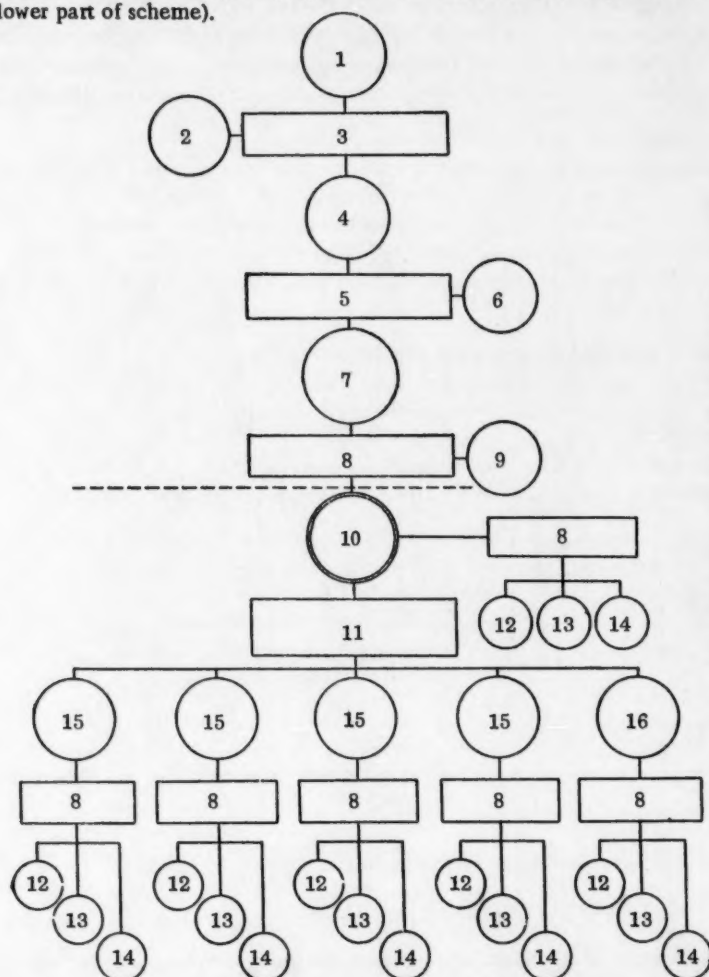


Fig. 1. Scheme for the isolation of compounds of high molecular weight from petroleum and for their separation into narrow fractions.

Key: 1) Romashkin petroleum; 2) distillate (below 325°); 3) vacuum distillate (bath temp. below 215°); 4) residue (above 325°); 5) precipitation of asphaltenes with 40 volumes of isopentane; 6) asphaltenes; 7) high-molecular-weight hydrocarbons and resins; 8) chromatography; 9) resins; 10) high-molecular-weight hydrocarbons; 11) molecular distillation (below 215°); 12) pcp; 13) mca; 14) cbca; 15) fraction I, fraction II, fraction III, fraction IV, fraction V; 16) residue.

The high-molecular-weight part of Romashkin petroleum had the following characteristics after molecular distillation: boiling range 325-625°; d_4^{20} 0.9050; n_D^{20} 1.5082; mol. wt. 351; sulfur content* 1.78%. Chromatographic analysis showed that in the original material the paraffin-cycloparaffin part amounted to 39% and the aromatic part to 59%. There were almost equal amounts of benzene and naphthalene homologs in the aromatic part (52.5% and 47.5% respectively).

If it is assumed that the sulfur compounds each contain not more than one sulfur atom, then the total amount of these was more than 18%. From the fact that sulfur was completely absent from the paraffin-cycloparaffin fractions, it follows that the sulfur compounds were all in the aromatic part, in which they were present in a concentration of 30%.

The molecular distillation was carried out in an apparatus of the still type, which, in consultation with the authors, was designed and constructed at the Experimental Factory of the Petroleum Institute of the Academy of Sciences. The molecular-distillation apparatus consisted of the following components: heater for the still in which the "free evaporation" of molecules of the mixture to be distilled occurred; condenser on which molecules evaporated from the surface of the mixture in the still condensed; a battery of receivers into which products collecting on the condenser surface passed; oil diffusion pump; backing pump; measuring devices. The distillation was carried out at a residual pressure of 10^{-4} mm, and the temperature at which the last fraction was taken was not above 215°. A single charge in the still of the molecular-distillation apparatus amounted to 25-30 g, and the duration of the distillation was 5-6 hours. In the distillation, four fractions of approximately equal amounts were collected, and the residue in the still formed the fifth fraction. The apparatus is shown diagrammatically in Fig. 2.

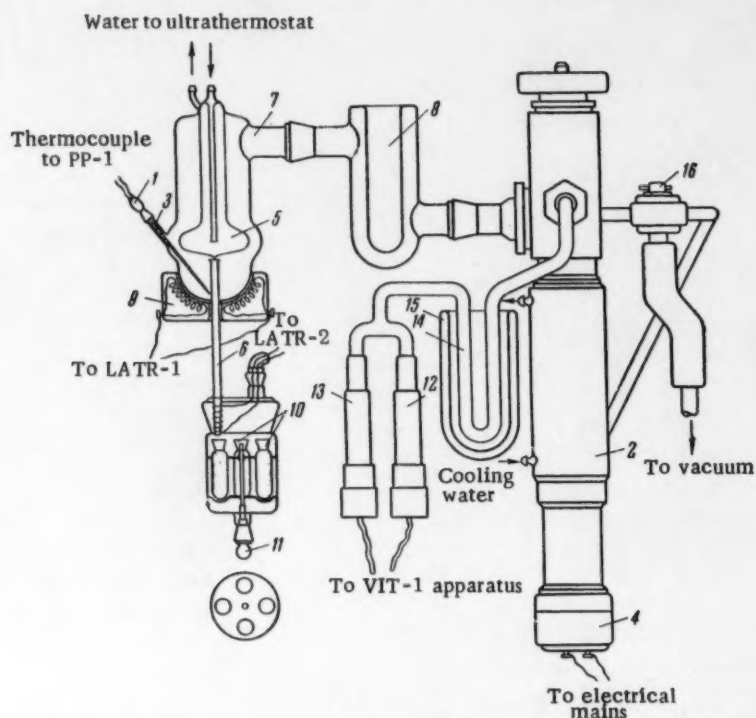


Fig. 2. Diagram of molecular-distillation apparatus.

Before the charge was placed in the apparatus, all the joints were greased and the system was checked for lack of leakage at a residual pressure of 10^{-5} mm. When it was confirmed that the apparatus was satisfactory in

*Sulfur contents were determined in all the investigated products by the method of double combustion in accordance with the directions given in [4].

this respect, the vacuum was broken, the joint carrying the thermocouple 1 was taken out, and 34-35 ml (previously weighed) of the mixture to be distilled was introduced with the aid of a funnel through the side tube 3. The side tube was then closed with the stopper carrying the thermocouple and the substance to be distilled was degassed; for this purpose, the still was heated to 60-70° with the electrical heater 9, with gradual lowering of pressure to 10^{-2} mm; in the degassing, the temperature of the condenser 5, which was connected with an ultra-thermostat, was kept at the same level as in the collection of Fraction I (20°).

After the degassing, the three-way tap 16 was turned to connect the system to the oil diffusion pump 2, which was heated by the electrical heater 4; a residual pressure of about 10^{-5} mm was attained, the temperature of the liquid to be distilled was gradually raised with the aid of an LATR-1 autotransformer, which maintained a rate of distillation of about three drops per minute. The lightest fractions evaporated from the liquid surface, condensed on the surface of the condenser 5, and then ran through the tube 6 into the test tube receiver 10. The stopper 11 carried a rod, to which a circle was fixed carrying four graduated test tubes; by rotation of the stopper, the test tubes were brought successively into a position under the tube leading from the condenser.

TABLE 1. Characteristics of Fractions Obtained in Molecular Distillation

Material	Content (% by weight)	Mol. wt.	d_4^{20}	n_D^{20}	Sulfur content (% by wt)	Content of sulfur com- pound (%)
Original mixture of hydro- carbons	100,0	351	0,9050	1,5082	1,78	19,5
Fraction I from molecular distillations	20,2	254	0,8876	1,4972	1,46	11,7
Fraction II from molecular distillations	19,1	306	0,8935	1,5010	1,56	14,9
Fraction III from molecular distillations	18,0	383	0,9047	1,5082	1,60	18,7
Fraction IV from molecular distillations	18,7	485	0,9138	1,5110	1,59	24,1
Residues from molecular dis- tillations	23,8	736	0,9272	1,5148	1,73	35,2
Losses	0,2	—	—	—	—	—

After the collection of Fraction I in the first test tube, the temperature of the condenser was raised to 30° and collection of the distillate was started in the second test tube. For the collection of Fraction III, the temperature of the condenser was raised to 40°, and for the collection of Fraction IV to 50°. Such gradual raising of the temperature of the condenser was necessary to make sure that the condensed fraction flowed off as completely and rapidly as possible into the receivers (the viscosities of the fractions rose sharply with rise in molecular weight).

Between the diffusion pump and the outlet 7, in the upper part of the still, there was a trap 8 filled with liquid nitrogen. The vacuum was measured with VIT-1 apparatus, fitted with a thermocouple electron tube LT-4M and an ionization electron tube MT-2 (12 and 13, respectively). The trap 14, which was immersed in liquid nitrogen in the Dewar vessel 15, was placed immediately before the tubes.

The highest temperature in the distillation (at the end of the distillation) reached 215°, and the electrical heater was then switched off and removed, and the residue from the distillation was allowed to cool to 80-90°. The vacuum was then broken, and the residue was poured through the side tube 3; the apparatus was washed out several times with benzene, which was later driven off from a water bath until the residue reached constant weight; this residue was then combined with the main residue. The losses in the distillation did not exceed 0.3-0.4%. Nothing condensed in the trap.

Table 1 gives approximately quantitative data on the distribution of the mixture of high-molecular-weight compounds of petroleum among the fractions obtained in molecular distillation, together with properties of the fractions obtained. In 18 distillations in this apparatus, we fractionated 511 g of high-molecular-weight hydrocarbons of Romashkin petroleum. The individual fractions varied fairly greatly in molecular weight (from 254 to 650).

TABLE 2. Structural-group Composition and Properties of Fractions of Hydrocarbons of High Molecular Weight Obtained by a Combination of Molecular Distillation and Chromatographic Separation

Material •	Mol. wt.	n_D^{20}	d_4^{20}	Sulfur content (% by weight)	Content of sulfur compounds (% by weight) on individual group of hydrocarbons	on fraction: on average with no account taken of resins formed during chromatography	Yield (% by weight on material taken for adsorption analysis)	Distribution of various groups of hydrocarbons among fractions (% by weight)	Structural-group analysis						
									Number of rings			Content of C atoms (%)			
									Total K ₀	Aromatic K _A	Cycloparaffin K _H	Cyclic C _K	Aromatic C _A	Cycloparaffin C _H	Paraffin C _P
Original material	295	1,4708	0,8468	Nil	Nil	18,2	39,0		1,4	0,3	1,1	34,3	8,2	26,1	65,7
mca	390	1,5066	0,9097	1,44	17,5		31,0		2,3	1,0	1,3	40,7	19,5	21,2	59,3
cbca	338	1,5623	0,9878	4,19	44,2		28,0	29,1	3,5	2,0	1,5	65,1	40,7	24,4	34,9
Fraction I from molecular distillation	269	1,4582	0,8280	Traces	Nil		50,0	10,6	1,1	—	1,1	30,9	0,8	30,1	69,1
mca	236	1,5069	0,9057	1,32	9,7		21,0	20,8	1,8	0,7	1,1	54,2	23,8	30,4	45,8
cbca	217	1,5739	0,9989	4,97	33,7		26,0	20,8	2,8	1,6	1,2	82,5	53,1	29,4	17,5
Fraction II from molecular distillation	302	1,4647	0,8395	Nil	Nil		51,0	27,0	1,2	0,1	1,1	30,1	3,8	26,3	69,9
mca	261	1,5137	0,9186	1,75	14,3		23,0	10,8	1,9	0,8	1,1	53,3	24,6	28,7	46,7
cbca	292	1,5794	1,0110	5,18	47,3		25,0	18,4	3,7	1,9	1,8	78,5	44,4	34,1	21,5
Fraction III from molecular distillation	360	1,4737	0,8465	Nil	Nil		48,0	25,5	1,5	0,5	1,0	32,2	40,7	21,5	67,8
mca	328	1,5150	0,9240	1,70	17,4		25,0	11,9	2,3	1,0	1,3	48,8	23,5	25,4	51,2
cbca	335	1,5688	0,9983	4,55	47,7		25,0	18,4	3,8	2,0	1,8	70,5	41,0	29,5	29,5
Fraction IV from molecular distillation	505	1,4761	0,8623	Nil	Nil		34,0	17,2	2,1	0,8	1,3	28,1	13,0	15,1	71,9
mca	450	1,5072	0,9121	1,42	20,0		34,0	15,3	2,5	0,9	1,6	38,9	16,6	22,2	61,2
cbca	404	1,5598	0,9875	4,00	50,5		29,0	10,0	4,1	2,1	2,0	62,8	35,5	27,3	37,2
Residue from molecular distillation	516	—	—	—	—		1,4	1,2	—	—	—	—	—	—	—
mca	642	1,5071	0,9128	1,33	26,7		71,0	51,4	3,2	1,1	2,1	37,1	13,9	23,2	62,9
cbca	641	1,5458	0,9689	2,98	59,7		20,0	22,4	5,1	2,6	2,5	48,6	26,9	21,7	51,4

* pcp = paraffin-cycloparaffin hydrocarbons; mca = monocyclic aromatics; cbca = condensed bicycloaromatics.

In sulfur content, the fractions obtained by molecular distillation differed very little and were very similar to the original mixture. Each of the fractions obtained by molecular distillation was then subjected to chromatographic separation on activated coarse-pore silica gel (ASK). The results of the chromatographic separation of the raw material and of each fraction from the molecular distillation are given in Table 2.

The use of molecular distillation enabled us to effect a much more detailed separation for the complex mixture of high-molecular-weight hydrocarbons of petroleum according to the sizes of the molecules under conditions precluding chemical change in the material to be separated. The further separation of the resulting fractions by chromatography was found to be extremely effective and enabled us to establish the existence of various regularities in the molecular-size distribution of hydrocarbons and sulfur compounds of various structural types in the high-molecular-weight part of Romashkin petroleum (see Table 2 and Figures 3 and 4). It was found that more than 80% of all the paraffin-cycloparaffin hydrocarbons contained in the original mixture were concentrated in the first three fractions, of which they formed 50%. The molecules of these compounds contained one or two cycloparaffin rings and contained no sulfur.

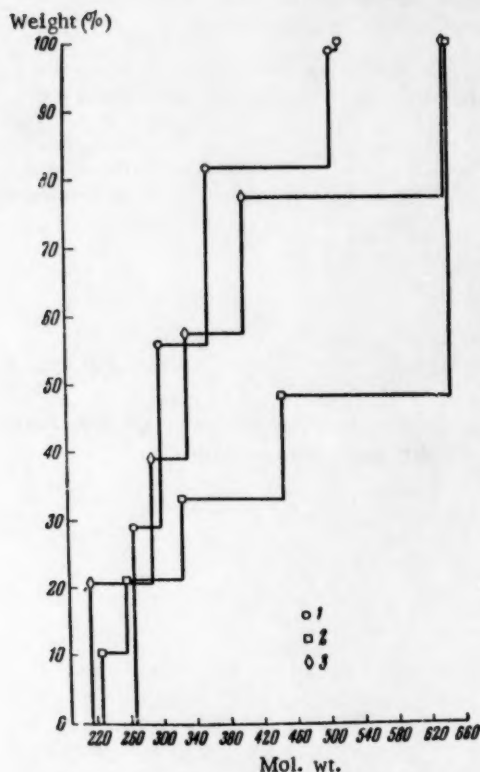


Fig. 3. Relation of fractional distribution of various groups of hydrocarbons to molecular weight: 1) Paraffins and cycloparaffins; 2) monocyclic aromatics; 3) condensed bicyclic aromatics.

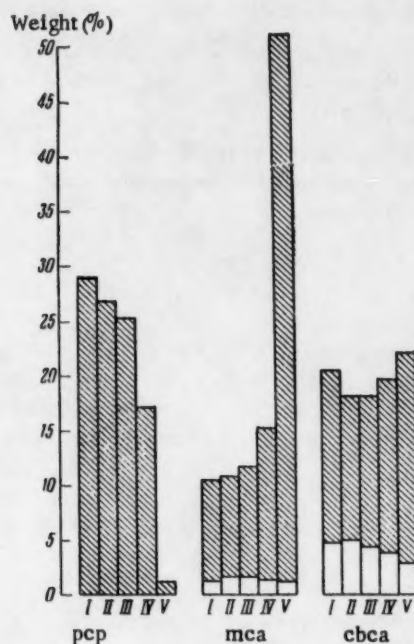


Fig. 4. Distribution of various groups of hydrocarbons among molecular distillation fractions, and their sulfur contents: The shaded areas indicate the distribution of various groups of hydrocarbons among the fractions (% by weight); the unshaded areas indicate sulfur contents (% by weight).

The bulk of the monocyclic aromatic hydrocarbons (51.4%) was concentrated in the residue, i.e., in that part of the original mixture which had the highest molecular weight. This fraction had a content of 71% of monocyclic hydrocarbons of average molecular weight 642. The remaining part of the monocyclic aromatics was

distributed evenly among the remaining four fractions. The total number of rings in the monocyclic aromatic hydrocarbons isolated from different fractions varied around 2 (1.8-2.5), and the aromatic hydrocarbons are to be assigned one ring, which indicates that these compounds were high homologs of benzene. Cyclic structures contributed 37-55% to all the carbon skeletons. The sulfur content varied within relatively narrow limits (1.33-1.75%) and corresponded to a content of sulfur compounds of 9.7-26.7%.

Compounds having molecules built from condensed aromatic nuclei were uniformly distributed among all the fractions. The total number of rings in them (Fractions II-IV) was about 4; of these the aromatics must be assigned two rings, which indicates that these compounds were naphthalene homologs. The first fraction (total number of rings 2.8, number of aromatic rings 1.6) and the last fraction (total number of rings 5.1, including 2.6 aromatic) show some departure from the above relation. The contribution of cyclic structures to the carbon skeleton of these compounds falls continuously from the first (82.5%) to the last (48.6%) fraction. The bulk of the sulfur compounds was concentrated in the compounds containing condensed aromatic nuclei in their molecules; in these fractions the sulfur-containing fractions amounted to 33.7-59.7%.

SUMMARY

1. It is shown that a combination of the methods of molecular distillation and chromatography is highly effective in the separation of mixtures of the high-molecular-weight compounds of petroleum into basic structural groups of compounds having similar molecular weights.
2. Monocyclic aromatic compounds have the highest molecular weights and are condensed in the last fraction of the molecular distillation, whereas the paraffin-cycloparaffin compounds are concentrated in the first two fractions.
3. The sulfur compounds are concentrated in the bicyclic aromatic compounds, which indicates that most of the sulfur of the high-molecular-weight compounds of petroleum is found in compounds of the bicyclic aromatic structural groups.

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TRANSFORMATIONS OF DIMETHYLCYCLOHEXANES IN PRESENCE OF A NICKEL-ALUMINA CATALYST AND HYDROGEN UNDER PRESSURE

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A comparatively large number of papers [1-5] has appeared in recent years in which reference is made to the use of metal catalysts in the transformations of cyclohexane and monoalkylcyclohexanes at high temperatures in presence of hydrogen at high pressure. In presence of metal catalysts and hydrogen at high pressure at 370-460° there occurs mainly dehydrogenation to the corresponding aromatic hydrocarbon, and this is accompanied by ring contraction with formation of alkylcyclopentanes. Moreover, one of us [2, 3, 5] has found that the dehydrogenation of methylcyclohexane at 460° in presence of various Group VIII metals and hydrogen at 20 atm is accompanied by demethylation with formation of cyclohexane and benzene, and also by methylation of the toluene formed, probably by the methylene radicals formed in the demethylation, with formation of xylenes. We have found no work in the literature on the transformations of dimethylcyclohexanes in presence of metal catalysts and hydrogen under pressure.

In a previous paper [6], we presented the results of the investigation of the transformation of individual hydrocarbons at elevated temperatures in presence of hydrogen under high pressure. In continuation of these investigations, we decided to study the behavior of the isomeric dimethylcyclohexanes at elevated temperatures in presence of hydrogen at high pressure and a nickel-alumina (10% Ni) catalyst. As a result of this work, we have shown that the main reaction in the catalytic transformations of the isomeric dimethylcyclohexanes is dehydrogenation and that the extent of this reaction increases when the pressure of hydrogen is reduced from 50 to 25 atm. This reaction is accompanied by hydrogenolysis of side groups with formation of methylcyclohexane and cyclohexane, and also of toluene and benzene.

EXPERIMENTAL

The dimethylcyclohexanes were prepared by hydrogenation of the corresponding xylenes in an autoclave at 170-180° in presence of Raney nickel; their properties after distillation through a column of 70-plate efficiency are given in Table 1.

TABLE 1. Properties of Original Dimethylcyclohexanes

Hydrocarbon	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Aniline point	Content (%) of	
					cis form	trans form
1,2-Dimethylcyclohexane	123-128,5(750)	1,4310	0,7859	43,2	85,0	15,0
1,3-Dimethylcyclohexane	119,5-122,5(743)	1,4238	0,7700	50,0	20	80
1,4-Dimethylcyclohexane	118,5-122,5(749)	1,4235	0,7699	48,2	60	40

All experiments were carried out over a 10% nickel-alumina catalyst at 460° in presence of hydrogen at 25 and 50 atm at a space velocity of 0.5 hour⁻¹, at a molar ratio of H₂:hydrocarbon of 5 : 1 in a flow-type apparatus [7] which permitted precise control of temperature, pressure of hydrogen, rate of passage of the original hydrocarbons, and relative amounts of hydrogen and original hydrocarbon. In each experiment, we took 150 ml of hydrocarbon, and 100 ml of catalyzate was taken for precision fractionation.

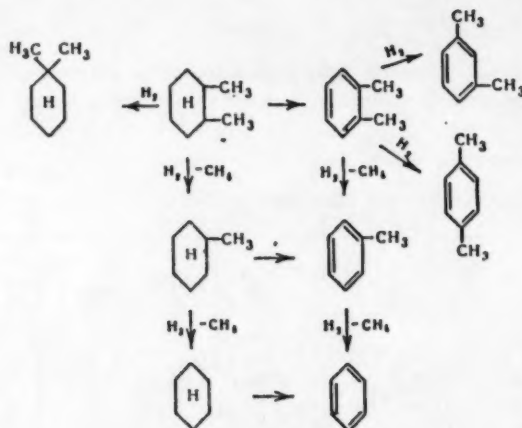
The catalyzates were analyzed by analytical fractionation through a column of 42-plate efficiency. Fractions containing cycloalkanes were separated by chromatographic adsorption on silica gel. Xylene fractions were analyzed by a method based on nitration [8], with subsequent gravimetric determination of m-xylene after crystallization of its trinitro derivative from acetone, and of p-xylene after crystallization of its 2,3- and 2,6-dinitro derivatives from ethanol. Fractions were analyzed also with the aid of Raman and ultraviolet spectra. The gas was analyzed in an Orsat-Lunge apparatus and chromatographically [9].

Catalytic Treatment of 1,2-Dimethylcyclohexane. The results obtained in the catalytic treatment of 1,2-dimethylcyclohexane are given in Table 2.

It follows from Table 2 that the main transformation of 1,2-dimethylcyclohexane under the given conditions consists in dehydrogenation to o-xylene. This reaction is accompanied by the demethylation of side groups with formation of toluene and benzene on the one hand, and methylcyclohexane and cyclohexane on the other.

The 79.5-80.5° (747 mm) fraction from Experiments 1 and 2 was subjected to chromatographic adsorption on silica gel; in this way, we isolated a naphthene part (b.p. 79.5-80°/750 mm; n_D^{20} 1.4263; d_4^{20} 0.7787; aniline point 31.1) which gave the Raman spectrum of cyclohexane. The aromatic part of this fraction consisted wholly of benzene. By adsorption on silica gel, toluene was removed from the 100-109.2° (747 mm) fraction from Experiments 1 and 2. The Raman spectrum showed that the dearomatized part of this fraction, which boiled over a narrow range (100-101°/750 mm), consisted mainly of methylcyclohexane. In addition, under these conditions 1,2-dimethylcyclohexane underwent some isomerization to 1,1-dimethylcyclohexane. The Raman spectrum of the 122-129° (747 mm) fraction of the catalyzate of Experiment 2 (n_D^{20} 1.4285; d_4^{20} 0.7802; aniline point 46.0) showed that it contained 20% of 1,1-dimethylcyclohexane and 80% of unchanged 1,2-dimethylcyclohexane. Under the same conditions there was a little isomerization of the o-xylene produced into m- and p-xylenes. The combined 137-142° fraction of the catalyzates of Experiments 1 and 2 (n_D^{20} 1.5030; d_4^{20} 0.8746) was analyzed by the method based on the nitration of xylenes. We found 80% of o-xylene, 10% of p-xylene, and 10% of m-xylene. It is probable that paraffins were also formed under our conditions. The head fractions of the catalyzates from Experiments 1 and 2 (b.p. 51-79.5°/747 mm) had n_D^{20} 1.3865 and d_4^{20} 0.6816. Comparison of their properties with data in the literature [10] gives reason to suppose that they contained isomeric C₆ paraffins and also, possibly, branched C₇ paraffins. In all experiments the gas consisted of methane and hydrogen.

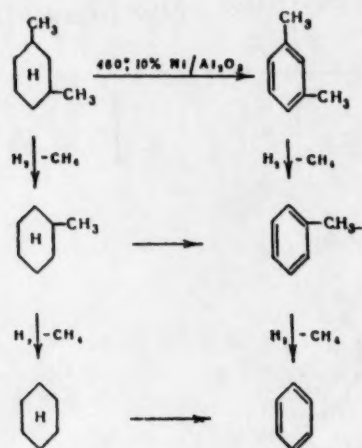
The main transformations of 1,2-dimethylcyclohexane in presence of a 10% nickel-alumina catalyst may be represented by the following scheme:



Catalytic Treatment of 1,3-Dimethylcyclohexane. The properties of the 1,3-dimethylcyclohexane catalyzates are presented in Table 3, which shows that the main products of the transformations of 1,3-dimethylcyclohexane are m-xylene, toluene, and benzene. Hence, as in the experiments with 1,2-dimethylcyclohexane, under the given conditions, there is a predominance of dehydrogenation and hydrogenolysis of methyl groups. It should be noted that at a hydrogen pressure of 25 atm, large amounts of toluene (32.3% on the catalyzate) and benzene (31.6% on the catalyzate) were formed. Demethylation with formation of methylcyclohexane and cyclohexane occurred to a much lesser extent.

The fractions containing cycloalkanes were analyzed in the same way as the corresponding fractions of the catalyzate of 1,2-dimethylcyclohexane. In the combined fraction of b.p. 138-138.5° (743 mm) of the catalyzates from Experiments 1 and 2 (n_D^{20} 1.4972; d_4^{20} 0.8641) we found only m-xylene. It follows that in the transformations of 1,3-dimethylcyclohexane in presence of a nickel-alumina catalyst isomerization of the m-xylene formed is not observed. This observation is in accord with the results of the catalytic treatment of m-xylene under the same conditions, which we carried out previously [11]. In the investigation cited it was shown that the xylene fraction consisted entirely of m-xylene. In all experiments the gas consisted of methane and hydrogen.

The results provide the basis for the following scheme of the transformations of 1,3-dimethylcyclohexane:



Catalytic Treatment of 1,4-Dimethylcyclohexane. The properties of the catalyzates of 1,4-dimethylcyclohexane are presented in Table 4, which shows that the catalytic treatment of 1,4-dimethylcyclohexane results mainly in dehydrogenation and the hydrogenolysis of methyl groups with formation of a large amount of toluene (31-36% on the catalyzate). In this case demethylation to benzene occurs to a much less extent than in the case of 1,3-dimethylcyclohexane.

The fractions isolated from the catalyzates obtained in Experiments 1 and 2, which contained naphthenes as well as aromatic hydrocarbons, were subjected to chromatographic adsorption on silica gel and spectroscopic analysis.

TABLE 2. Properties of 1,2-Dimethylcyclohexane Catalyzates

Expt.	H ₂ pres- sure (atm)	Yield of liquid catalyzate (wt. %)	Properties of catalyzate		Dehydro- genation (% on catal- yzate)	Composition of catalyzate (wt. %)								
			n_D^{20}	d_4^{20}		Benzene	Toluene	o-Xylene	m-Xylene	p-Xylene	Cyclo- hexane	Methyl- cyclohex- ane	1,1-Di- methyl- cyclohex- ane	unchanged 1,2-Dimeth- ylcyclohex- ane
1	25	89.2	1.4918	0.8573	90.7	10.0	17.0	62.7	0.5	0.5	3.0	5.0	—	1.0
2	50	85.9	1.4705	0.8274	68.0	7.0	12.0	46.4	1.4	1.2	4.5	10.0	2.0	15.0

It was shown that they contained methylcyclohexane and cyclohexane. Again in the transformations of 1,4-dimethylcyclohexane, isomerization of the p-xylene produced does not occur. The combined fraction of b.p. 137-138° of the catalyzates from Experiments 1 and 2 (n_D^{20} 1.4958; d_4^{20} 0.8611) consisted entirely of p-xylene. In all experiments the gas consisted of methane and hydrogen.

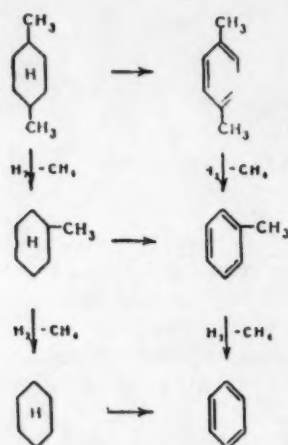
TABLE 3. Properties of 1,3-Dimethylcyclohexane Catalyzates

Expt.	H_2 pressure (atm)	Yield of liquid catalyzate (wt. %)	Properties of catalyzate		Dehydrogenation (% on catalyzate)	Composition of catalyzate (% by wt.)					
			n_D^{20}	d_4^{20}		Benzene	Toluene	Cyclohexane	Methylcyclohexane	m-Xylene	unchanged 1,3-dimethylcyclohexane
1	25	82.1	1.4906	0.8577	90.5	31.6	32.3	3.7	4.8	26.6	1.0
2	50	90.0	1.4760	0.8382	76.0	15.0	25.7	8.0	11.0	35.1	5.0

TABLE 4. Properties of 1,4-Dimethylcyclohexane Catalyzates

Expt.	H_2 pressure (atm)	Yield of liquid catalyzate (wt. %)	Properties of catalyzate		Dehydrogenation (% on catalyzate)	Composition of catalyzate (% by wt.)					
			n_D^{20}	d_4^{20}		Benzene	Toluene	p-Xylene	Cyclohexane	Methylcyclohexane	unchanged 1,4-dimethylcyclohexane
1	25	89.8	1.4830	0.8617	83.0	6.5	35.9	40.6	2.0	4.0	11.0
2	50	89.4	1.4720	0.8307	71.2	6.9	31.1	39.2	3.5	4.9	10.0

Scheme of the transformations of 1,4-dimethylcyclohexane:



The Raman spectrum analysis was carried out by Yu. P. Egorov, to whom the authors express their thanks.

SUMMARY

1. An investigation was made of the catalytic transformations of 1,2-, 1,3-, and 1,4-dimethylcyclohexanes at 460° in presence of a nickel-alumina catalyst and hydrogen at pressures of 25 and 50 atm.
2. The main reaction occurring in the transformations of the dimethylcyclohexanes was dehydrogenation to the corresponding xylenes, and the extent to which this occurred diminished with increase in the pressure of hydrogen.
3. Dehydrogenation was accompanied by the hydrogenolysis of methyl groups with formation, on the one hand, of toluene and benzene and, on the other, of methylcyclohexane and cyclohexane.
4. In the catalytic treatments of 1,3- and 1,4-dimethylcyclohexanes under the given conditions, 32-36% of toluene on the catalyzate was formed. The transformations of 1,3-dimethylcyclohexane went still further and were accompanied by the formation of about 30% of benzene on the catalyzate.

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*Original Russian pagination. See C. B. translation.

DEHYDROGENATION OF HYDROCARBONS OVER ALUMINA-CHROMIA AND ALUMINA-CHROMIA-POTASSIA CATALYSTS PREPARED IN VARIOUS WAYS

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It is known that the best catalysts for the dehydrogenation of gaseous paraffins are alumina-chromia catalysts [1, 2]. The use of these catalysts in the preparation of butenes from butane has been introduced on an industrial scale [1-3]. Investigations of recent years, both ours and those of others [4], have shown also that alumina-chromia catalysts are active also for the dehydrogenation of pentane and isopentane. However, the dehydrogenation of paraffins containing six or more carbon atoms in their molecules is accompanied by their aromatization [5], and n-alkanes generally give a much larger amount of aromatic hydrocarbons than of unsaturated hydrocarbons.

For the dehydrogenation of C_4 - C_5 hydrocarbons alumina-chromia catalysts are generally used with the addition of oxides of other metals. For this purpose, use is most frequently made of potassium oxide, which is introduced as KOH [6] or as potassium salts $K_2Cr_2O_7$ [7] and K_2CO_3 [8], which decompose with heat. The effect produced by an addition of potassium oxide to an alumina-chromia catalyst on the dehydrogenation of hydrocarbons has not yet been finally explained. Lyubarskii and Ermakova [9] consider that the presence of alkali-metal oxides in alumina reduces the thermal stability of an alumina-chromia catalyst in the dehydrogenation of butane and also increases the deposition of carbon.

There are many methods of preparing alumina-chromia catalysts; these are described in the above-cited reviews [1, 2, 5] and in many patents. We set ourselves the task of determining the effect of the method of preparing alumina-chromia and alumina-chromia-potassia catalysts on their activities and stabilities in the dehydrogenation of isopentane, hexane, and cyclohexane. We were interested also in the possibility of changing the relative amounts of unsaturated and aromatic hydrocarbons formed in the catalytic treatment of hexane in the direction of increase in the content of unsaturateds and reduction in the content of aromatics by variation in the method of preparing the catalyst. With the object of carrying out our task we prepared eight samples of alumina-chromia-potassia catalyst of composition 90.7 moles percent Al_2O_3 , 5.6 moles percent Cr_2O_3 , and 3.7 moles percent K_2O and two alumina-chromia catalysts without K_2O , but with the same proportions of Al_2O_3 and Cr_2O_3 as the alumina-chromia-potassia catalysts. The transformations of isopentane, hexane, and cyclohexane were studied under identical conditions in presence of these catalysts. In addition, the transformations of these hydrocarbons were investigated over Al_2O_3 , $Al_2O_3 + K_2O$, and Cr_2O_3 to determine the parts played by the separate components; the thermal transformations of the hydrocarbons (over quartz) were also studied.

It was found that the investigated methods of preparing alumina-chromia-potassia catalysts varied in their effects on activity and stability in the reactions concerned. The activities and stabilities of alumina-chromia catalysts were changed by the introduction of K_2O . It was shown also that it is possible in principle to change the relative amounts of unsaturated and aromatic hydrocarbons formed from hexane by the use of catalysts prepared in different ways.

EXPERIMENTAL

Catalysts. For the preparation of catalysts by the impregnation method, we used alumina in the form of 2-4 mm grains roasted at 500° for two hours. The alumina was impregnated with solutions of chromium and potassium salts, left for one day in the air, and then heated in a drying oven at 150° for 24 hours and in a muffle at 500° for ten hours. In this way, we prepared Catalysts 2, 4, 6, 7, 8, 10, 11, and 13. Catalysts 5 and 9 were prepared by coprecipitation with 10% ammonia from 1 M solutions of aluminum and chromium salts. Catalyst 12, was prepared from commercial alumina, ammonium dichromate, and potassium carbonate; chromium oxide was prepared by the decomposition of ammonium dichromate with heat. After thermal treatment in the drying oven and muffle, all catalysts were heated in the catalysis furnace in a stream of air at 700° for ten hours. Catalysts 3, 5, 9, and 12 were molded into tablets 2 mm thick and 4 mm in diameter.

We therefore used the following catalysts: 1) Al_2O_3 ; commercial activated product. 2) $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}$ (96.1 : 3.9 moles %); this catalyst was prepared by the impregnation of alumina with KNO_3 solution. 3) Cr_2O_3 ; this was prepared by the roasting of ammonium dichromate and subsequent formation into tablets. 4) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ (94.2 : 5.8 moles %); alumina was impregnated with ammonium dichromate solution. 5) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ (94.2 : 5.8 moles %); a precipitated catalyst. 6) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ (90.7 : 5.6 : 3.7 moles %); alumina was impregnated with a solution of potassium and ammonium dichromates; this catalyst was used in previous investigations [4, 10]; all the remaining catalysts had the same composition as Catalyst 6. 7) The catalyst was prepared by the impregnation of alumina with a solution of potassium nitrate and ammonium dichromate. 8) The impregnation of alumina was carried out with a solution of chromic nitrate and potassium nitrate. 9) Dry potassium nitrate was added to dry Catalyst 5, which was in the form of a powder; the mixture was carefully ground in a mortar and then formed into tablets. 10) This was the same catalyst as Catalyst 7, but potassium carbonate was taken instead of potassium nitrate. 11) This was the same catalyst as Catalyst 10, but potassium hydroxide was taken instead of potassium carbonate. 12) A mixture of chromic nitrate, potassium carbonate, and commercial alumina with a little water, ground in a mortar for 20 hours to give a homogeneous mass; this was dried and formed into tablets. 13) Chromic anhydride and potassium carbonate were taken for the impregnation of alumina.

Original Hydrocarbons. Isopentane, hexane, and cyclohexane were treated with concentrated sulfuric acid, washed with water, dried with calcium chloride, and distilled over sodium through a column of 42-plate efficiency. The hydrocarbons then had constants in accord with data in the literature [11].

Experimental Procedure. The catalytic treatment of the hydrocarbons was carried out at atmospheric pressure at 500° at a space velocity of 0.5 hour⁻¹. The amount of catalyst in the tube was 30 ml. In each experiment, after the catalyst had been heated to the necessary temperature, the air was displaced from the system with nitrogen. Then, to activate the catalyst and fill the system with reaction products, 7 ml of the hydrocarbon was introduced into the tube from a sprinkler buret at a space velocity of 0.5 hour⁻¹, and the experiment was started immediately, with the passage in all cases of 100 ml of the hydrocarbon over the catalyst.

After each experiment the catalysts were regenerated in a stream of air at 700° for 5-6 hours. Parallel experiments were carried out under the same conditions, and the results were generally in good agreement. The reaction products were analyzed as in our previous investigations [4, 10]. The aromatics contents of cyclohexane catalyzates were determined from the refractive index. To determine the relation of catalyst activity to the duration of the reaction separate portions of the catalyzate, each corresponding to 10 ml of the original hydrocarbon, were analyzed at various times throughout a seven-hour experiment. Table 1 presents data characterizing the compositions of the liquid catalyzates and gases obtained in the catalytic treatment of 100-ml portions of hydrocarbons over different catalysts. Fig. 1 shows the relation of the activities of catalysts in the dehydrogenation of isopentane, hexane, and cyclohexane and in the dehydrocyclization of hexane to the time during which the catalysts are in work. Table 2 gives the yields of unsaturated and aromatic hydrocarbons (on the amount of hydrocarbons (on the amount of hydrocarbon passed and on the amount decomposed) and also the specific surfaces of the catalysts [12].

Tables 1 and 2 show that the differences in the methods of preparing the catalysts have the least effect on the dehydrogenation of isopentane. Actually, over all the alumina-chromia-potassia catalysts (6-13), apart from the coprecipitated Catalyst 9, the yields of isopentenes from isopentane vary in the range 38-41% (on the hydrocarbon passed) irrespective of the method of preparation and of introduction of K_2O . Over Catalyst 9, the yield is 29%.

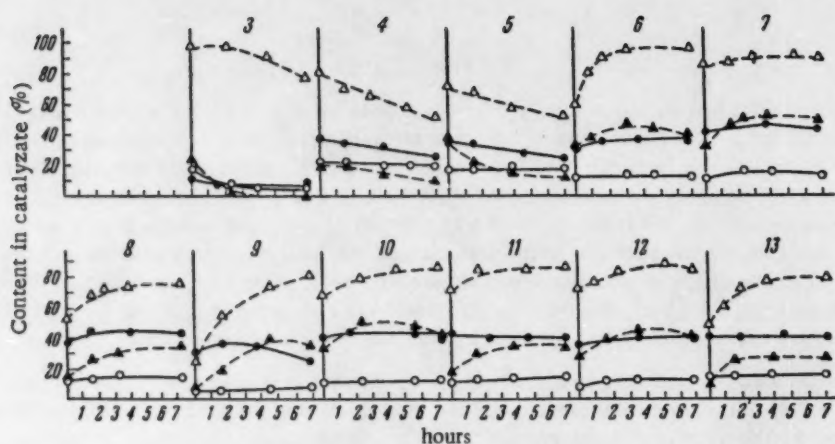


Fig. 1. Relation of contents of unsaturateds (● - from isopentane; ○ - from hexane) and of aromatics (▲ - from hexane; △ - from cyclohexane) to time of catalysts in work: 3) Cr_2O_3 ; 4) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ (pptd); 5) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ (impregtd); 6) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ [$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$]; 7) same, but KNO_3 instead of $\text{K}_2\text{Cr}_2\text{O}_7$; 8) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ [$\text{Cr}(\text{NO}_3)_3$ and KNO_3]; 9) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ (pptd); 10) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ [$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CO}_3$]; 11) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ [$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 + \text{KOH}$]; 12) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ (grinding of moist salts); 13) $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ ($\text{CrO}_3 + \text{K}_2\text{CO}_3$).

However, the method of preparation of alumina-chromia-potassia catalysts and the method of introducing K_2O have a much greater effect on their dehydrocyclizing power. Thus, in presence of Catalysts 6, 7, 10, and 12, the yields of benzene obtained from hexane are 37-39% on the amount of hydrocarbon passed, whereas, over Catalysts 8, 9, 11, and 13, they fall to 24-28%.

It is interesting that the yields of unsaturateds obtained from hexane in presence of all the alumina-chromia-potassia catalysts, except Catalyst 9, are close in value (9-13% on the hexane passed), irrespective of the yields of benzene. Over Catalyst 9, this yield is 5%. In the dehydrogenation of cyclohexane over alumina-chromia-potassia catalysts, the yields of benzene vary from 56% to 78%. Hence, the effect of the method of preparation of the catalysts on the extent to which this reaction occurs is still greater than its effect on the dehydrocyclizing power.

On examination of the results obtained over the alumina-chromia-catalysts 4 and 5, on the one hand, and over the alumina-chromia-potassia catalysts 6-13, on the other, it is seen that the addition of K_2O by various methods to the alumina-chromia catalysts, except Catalyst 9, has a favorable effect in increasing the yields of unsaturateds from isopentane (27-30% on the isopentane passed over alumina-chromia and 37-40% over alumina-chromia-potassia) and of benzene from hexane (14-17% and 22-38%, respectively) and from cyclohexane (50-51% and 59-78%, respectively). However, the yields of unsaturateds from hexane over alumina-chromia catalysts are 1.5-2 times as high as over alumina-chromia-potassia catalysts (16-20% over alumina-chromia and 9-13% over alumina-chromia-potassia).

The results obtained over alumina-chromia catalysts (K_2O absent) prepared in various ways vary very little, though their specific surfaces vary considerably, e.g., the specific surface of Catalyst 4 is $154 \text{ m}^2/\text{g}$, whereas that of Catalyst 5 is $220 \text{ m}^2/\text{g}$. Nevertheless, over Catalyst 4, which was prepared by impregnation, the ratio of the amounts of unsaturated and aromatic hydrocarbons formed from hexane is 1.5 times as great as over the coprecipitated catalyst. The catalyst prepared in presence of Catalyst 4 contained 23% of unsaturated and 16% of aromatic hydrocarbons; its fractionation through a column and analysis of the fractions then isolated showed that almost all of the unsaturateds consisted of C_6 hydrocarbons. In general, however, the ratio of unsaturated and aromatic hydrocarbons obtained from hexane depends on the method of preparation of the catalyst, as can be seen from Table 2. Introduction of K_2O in various ways into alumina-chromia catalysts has a favorable effect on

TABLE 1. Properties of Liquid Catalyzates and Gases

Catalyst	Hydrocarbon	Yield of liquid catalyzate (%)	n_D^{20}	Content in catalyzate (% kg wt) of		Amount of gas (liters at STP)	Composition of gas (% by vol.)		
				unsaturated hydrocarbons *	aromatic hydrocarbons		H ₂	C _n H _{2n}	C _n H _{2n+2}
Quartz	Isopentane	90,6	1,3435	6,7	—	2,850	12,7	22,5	64,8
	Hexane	73,8	1,3740	10,5	Traces	12,100	5,0	50,0	45,0
	Cyclohexane	95,0	1,4250	3,8	»	0,910	47,0	29,2	23,8
1	Isopentane	95,4	1,3540	1,8	—	0,630	68,1	7,6	24,3
	Hexane	96,0	1,3745	1,8	Traces	0,650	87,0	8,0	5,0
	Cyclohexane	96,6	1,4305	9,5	8,0	8,850	79,5	3,2	17,3
2	Isopentane	92,7	1,3530	2,1	—	0,380	34,3	31,0	34,7
	Hexane	92,3	1,3745	1,8	1,0	0,660	10,8	34,4	54,8
	Cyclohexane	96,2	1,4255	1,0	—	0,200	15,5	10,7	73,8
3	Isopentane	96,5	1,3550	7,3	—	1,640	85,0	2,6	12,4
	Hexane	94,9	1,3800	6,8	4,0	5,710	80,1	7,2	12,7
	Cyclohexane	77,0	1,4910	Traces	90,4	56,760	100,0	—	—
4	Isopentane	90,9	1,3638	31,0 (1,2)	—	10,810	85,5	1,0	13,5
	Hexane	86,9	1,3950	22,6	16,0	18,270	90,6	0,4	9,0
	Cyclohexane	82,7	1,4650	Traces	61,0	42,640	96,2	0,5	3,3
5	Isopentane	88,2	1,3625	30,5 (0,3)	—	11,220	83,1	1,5	15,4
	Hexane	84,8	1,4000	18,6	19,8	21,220	85,2	2,4	12,4
	Cyclohexane	86,1	1,4640	2,3	59,8	45,080	97,0	0,0	3,0
6	Isopentane	94,5	1,3655	38,8 (1,3)	—	9,050	88,0	0,7	11,3
	Hexane	86,8	1,4220	13,7	42,6	34,400	95,0	0,6	4,4
	Cyclohexane	83,5	1,4900	Traces	89,3	57,380	99,0	0,3	0,7
7	Isopentane	91,2	1,3665	39,3 (1,2)	—	12,840	86,7	2,0	11,3
	Hexane	83,1	1,4315	10,9	46,0	37,090	92,8	1,2	6,0
	Cyclohexane	81,4	1,4890	Traces	88,2	55,900	99,0	0,4	0,6
8	Isopentane	94,2	1,3660	41,0 (1,5)	—	11,280	89,0	0,9	10,1
	Hexane	82,6	1,4110	14,4	34,0	29,420	90,6	1,2	8,2
	Cyclohexane	84,4	1,4730	1,1	70,6	46,740	96,6	1,1	2,3
9	Isopentane	87,9	1,3645	31,8 (1,2)	—	11,070	86,7	2,0	11,3
	Hexane	87,0	1,4052	5,7	27,6	25,320	92,8	1,2	6,0
	Cyclohexane	87,7	1,4675	Traces	64,2	43,230	98,8	1,2	0,0
10	Isopentane	92,1	1,3660	40,2 (1,9)	—	10,140	91,1	0,0	8,9
	Hexane	80,2	1,4260	13,3	42,4	38,700	96,2	0,0	3,8
	Cyclohexane	84,2	1,4800	Traces	78,4	51,500	98,7	1,3	0,0
11	Isopentane	92,5	1,3660	39,3 (1,4)	—	10,160	87,8	1,3	10,9
	Hexane	86,7	1,4122	13,6	32,6	28,640	93,5	1,2	5,3
	Cyclohexane	74,5	1,4860	0,8	85,0	54,520	98,2	0,0	1,8
12	Isopentane	92,1	1,3665	41,0 (0,4)	—	10,800	90,0	1,9	8,1
	Hexane	84,9	1,4210	13,1	45,8	30,270	93,9	3,5	2,6
	Cyclohexane	83,8	1,4832	Traces	82,0	52,280	98,7	1,3	0,0
13	Isopentane	94,6	1,3660	39,7 (1,5)	—	10,510	88,5	0,0	11,5
	Hexane	85,8	1,4090	15,4	25,6	27,910	91,0	2,0	7,0
	Cyclohexane	80,3	1,4780	1,8	76,2	46,870	98,8	1,2	0,0

* The content of unsaturated hydrocarbons in the hexane and cyclohexane catalyzates, and also in isopentane catalyzates obtained over quartz and Catalysts 1, 2, and 3, is calculated on the basis of C₆ and C₅ monoolefins, no account being taken of any dienes or gaseous unsaturated hydrocarbons formed; for the other isopentane catalyzates, the contents of isopentenes and isoprene (in parentheses) are given separately.

their stabilities in the dehydrogenation of isopentane and cyclohexane and also in the dehydrocyclization of hexane, as is clearly seen from Fig. 1. Actually, the activities of alumina-chromia catalysts fall during the experiments, whereas the activities of alumina-chromia-potassia catalysts either remain constant, rise, or pass through a maximum. The yields of unsaturated hydrocarbons obtained from hexane in presence of any of the catalysts vary little with time in the course of an experiment and do not depend on the yields of benzene.

TABLE 2. Yields of Dehydrogenation and Dehydrocyclization Products (%) by Weight on the Amount of Hydrocarbons Passed and on the Amount of Hydrocarbon Decomposed)

Catalyst	Specific surface (sq. m/ g)	Unsaturateds (calculated as monoolefins)				Benzene			Ratio of yields of unsaturateds and aromatics (on hexane passed)
		from isopentane		from hexane		from hexane		from cyclohexane	
		on h.c. passed	on h.c. decomposed	on h.c. passed	on h.c. decomposed	on h.c. passed	on h.c. decomposed	on h.c. decomposed	
Quartz	—	6,0	39,0	7,7	22,7	Traces	Traces	Traces	3,00
1	129	1,7	27,0	1,7	30,0	Traces	7,7	38,0	1,70
2	148	1,9	20,7	1,7	18,1	Traces	Traces	Traces	1,70
3	18	7,0	67,0	6,5	42,3	3,8	69,6	75,2	1,71
4	154	29,5	76,4	19,6	42,1	13,9	50,4	74,5	1,41
5	220	27,3	69,8	15,8	33,4	16,8	51,5	76,4	0,94
6	143	38,2	87,5	11,9	19,2	37,0	74,6	81,9	0,32
7	144	38,6	81,5	9,1	14,2	38,2	77,8	80,7	0,24
8	149	40,8	87,6	11,9	20,7	28,1	59,6	78,3	0,42
9	171	29,2	70,7	5,0	12,0	24,0	56,3	82,1	0,21
10	131	39,1	83,2	10,7	16,6	34,0	66,0	80,7	0,32
11	129	37,9	83,5	11,9	22,1	28,3	63,3	70,8	0,48
12	150	38,2	83,0	11,1	17,1	38,9	68,7	80,9	0,29
13	153	39,3	88,0	13,2	26,7	22,0	61,2	74,4	0,60

It will be seen that the method of preparation affects the specific surface of an alumina-chromia-potassia catalyst; it varies from 129 to 121 m²/g. However, the variation in specific surface has little effect on the activities and stabilities of the catalysts. An exception is the alumina-chromia-potassia catalyst 9, which was prepared by coprecipitation of aluminum and chromium hydroxides, admixture of potassium carbonate, and thermal decomposition; it was found to be less active in the dehydrogenation of isopentane and the dehydrocyclization of hexane, though its specific surface was the greatest, namely 171 m²/g. The other alumina-chromia-potassia catalysts have a smaller specific surface (129-153 m²/g) and are more active than Catalyst 9, irrespective of the value of the specific activity. It should be noted that the specific activities of Catalysts 10 and 11 are almost the same as that of the original alumina. The other catalysts, which were prepared from commercial alumina (2, 4, 6, 7, 12, and 13), have greater specific surfaces than the alumina.

It will be seen from Tables 1 and 2 that over quartz at 500° isopentane, hexane, and cyclohexane give 4-10% of unsaturated hydrocarbons; also, the gases liberated in the catalytic process are poorer in hydrogen and contain more unsaturated hydrocarbons and methane than the gases formed in most of the other experiments. The catalyzate obtained over quartz was fractionated through a column of 42-plate efficiency. The fractions so obtained were analyzed. It was found that the catalyzate contained 1% of C₅ and 3% of C₆ unsaturated hydrocarbons. The gas liberated from the catalyzate consisted of 95% of unsaturated hydrocarbons and 5% of methane. Hence, in presence of quartz hexane is extensively cracked; only 3% of C₆ unsaturated hydrocarbons is formed, and only traces of aromatic hydrocarbons.

Alumina is not a very active dehydrogenation catalyst: Isopentane and hexane give 2% of unsaturateds, and cyclohexane gives 10% of unsaturateds. Under the conditions investigated alumina has scarcely any catalytic action on dehydrocyclization. In presence of alumina, cracking of the hydrocarbons goes to a much less extent than in presence of quartz. Al₂O₃ + K₂O gave similar results to alumina alone with respect to activity in the dehydrogenation of isopentane and hexane. However, this catalyst is less active in the dehydrogenation of cyclohexane. The curves for Al₂O₃ and Al₂O₃ + K₂O are absent from Fig. 1, because all the curves are parallel to the axis of abscissae.

Chromic oxide has low activity in the dehydrogenation of isopentane and hexane and high activity in the dehydrogenation of cyclohexane, though this activity falls with time. One of the causes of the low activity of chromic oxide is probably the screening of the surface, which is only 18 m²/g, by condensation products formed in the catalytic treatment of unsaturated hydrocarbons. A very much smaller amount (traces) of unsaturateds is formed from cyclohexane, and on this account, the activity of the catalyst is maintained at a higher level in aromatization reactions.

It is noteworthy that for most of the catalysts the dehydrogenation and aromatization curves are not parallel. Hence, the rates of the two competing reactions change in different ways with the passage of time. This view is not in accord with the basic experimental premises on which Steiner [13] based his conclusion that the active centers in oxide catalysts for the dehydrogenation and dehydrocyclization of paraffins are identical. This investigator considers that poisoning lowers the rate of dehydrogenation to approximately the same extent as it lowers the rate of dehydrocyclization.

SUMMARY

1. An investigation was made of the effect of the method of preparation of alumina-chromia and alumina-chromia-potassia catalysts on their dehydrogenating and dehydrocyclizing activities.
2. The methods investigated for the preparation of catalysts affect the course of the dehydrogenation of isopentane least of all. In the dehydrocyclization of hexane the dependence is more marked. The dependence on the method of preparing the catalysts is still more marked in the dehydrogenation of cyclohexane.
3. The introduction of K₂O into alumina-chromia catalysts, however this may be effected, raises their activities and stabilities in the dehydrogenation of isopentane and cyclohexane and also in the dehydrogenation of hexane; it also reduces the yields of unsaturated hydrocarbons from hexane.
4. Of all the catalyst investigated, the best from the point of view of the obtaining of maximum yields of hexenes and the minimum yields of benzene is the alumina-chromia catalyst prepared by impregnation of alumina with ammonium dichromate solution (23% of unsaturated hydrocarbons and 16% of benzene).

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POISONING OF A Pt CATALYST BY THIOPHENE UNDER REFORMING CONDITIONS
COMMUNICATION 1. EFFECT OF THE CONCENTRATION OF THIOPHENE

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A large amount of material has now accumulated in the literature [1, 2] on the poisoning of catalysts in hydrogenation and dehydrogenation processes proceeding at atmospheric pressure. It has been shown in numerous investigations [1-3] that for the suppression of the activity of catalysts, particularly those containing Group VIII metals, an extremely small amount of catalyst poison is needed. Among these poisons for metal catalysts, some of the most powerful are sulfur-containing organic compounds. The toxicity of these for platinized charcoal under the conditions of dehydrogenation catalysis was observed by Zelinskii and co-workers [4,5], who showed that this phenomenon is reversible and gave a scheme for the mechanism of the poisoning and regeneration of these catalysts.

In a study of the effect of thiophene on Ni-MgO catalysts in the dehydrogenation of cyclohexane and the hydrogenation of benzene, Rubinshtein and Pribytkova [6, 7] showed that catalysts of high dispersity are more stable to the action of the poison. On the basis of the relation of the activation energy for the dehydrogenation of cyclohexane to the amount of poison introduced, the authors drew conclusions concerning the mechanism of the poisoning of the catalysts (in this case, chemisorption) and the heterogeneity of their surfaces.

In the investigations of one of us and Shuikin [8, 9], a study was made of the poisoning of platinum deposited on activated charcoal, porous glass, and silica gel, and of nickel deposited on zinc oxide and alumina. The poisons used were 1-propanethiol, 3-methyl-1-butanethiol, thiophene, tetrahydrothiophene, diethyl sulfide, diisopentyl sulfide, hydrogen sulfide, and carbon disulfide. The experiments were carried out in a flow system at 280-300° under the conditions for the dehydrogenation of cyclohexane at atmospheric pressure. As a result of these investigations, it was shown that 1) the character of the poisoning of catalysts and also their amenability to regeneration depends essentially on the chemical nature of the carrier; 2) the structure of the sulfur compounds, which under these conditions are converted into hydrogen sulfide, has little effect on the rate of deactivation of the catalysts; 3) the activation energy for the dehydrogenation of cyclohexane, both over freshly prepared and over poisoned catalysts (with the exception of nickel catalysts), remains almost constant, whereas the value of the preexponential term in the Arrhenius equation falls to a fraction of its initial value; 4) according to x-ray structure analysis, carried out both on freshly prepared and on poisoned platinum catalysts, the phase compositions of the catalysts do not change and only the crystalline phase of platinum is present.

On the basis of the results, we concluded that the poisoning of platinum catalysts proceeds by the mechanism of blocking of active centers, whereas in the case of Ni-Al₂O₃, it proceeds by a chemisorption mechanism and, in the case of Ni-ZnO, it proceeds as a result of change in the chemical nature of the carrier due to partial formation of ZnS, which explains the considerable stability of the latter catalyst in comparison with Ni-Al₂O₃.

In recent years, platinum deposited on various carriers (Al₂O₃, SiO₂, Al₂O₃-SiO₂) is finding more and more industrial application for the treatment of sulfur-containing gasoline and ligroin fractions, both with the object of producing concentrates of aromatic hydrocarbons, and with the object of improving their octane ratings. All

these processes, under the names of platforming, catforming, ultraforming, etc., are carried out at an elevated pressure of hydrogen, at 450-510°, and with recirculation of the gases formed. In view of the fact that more than one-half of the petroleum now obtained and refined in the USSR is derived from the sulfur-containing petroleum of the Volga-Urals district, the investigation of the poisoning of catalysts by sulfur-containing compounds under conditions close to those used in industry has acquired not only theoretical but also considerable practical interest.

Only a few investigations have been reported on the effect of sulfur-containing compounds on platinum catalysts, working at elevated temperatures under high pressures of hydrogen in apparatus of the flow type. Thus, Heinemann and co-workers [10] investigated the effect of thiophene, benzenethiol, 1-butanethiol, diethyl sulfide, and elementary sulfur on the extents of the dehydrogenation of cyclohexane and of the formation of benzene from methylcyclopentane in presence of a platinum catalyst at 510°, under 20 atm of hydrogen, and with a ratio of hydrocarbon to hydrogen of 1 : 4; the space velocity for the feed of hydrocarbons containing a definite amount of sulfur-containing compounds was 6 hour⁻¹. The experiments showed that the yield of benzene is reduced on the average by 40% if cyclohexane containing 0.5% of sulfur is introduced into the reaction. Approximately the same reduction in the yield of benzene was observed in the dehydroisomerization of methylcyclopentane. The authors showed that all sulfur-containing compounds are converted into hydrogen sulfide and that the desulfurizing activity of the catalyst is preserved even after its dehydrogenating power has fallen. These experiments confirmed the results obtained previously by other authors [4, 8]. Also, it was shown in the same investigation that, other conditions being constant, raising the total pressure of hydrogen favors maintenance of the activity of the catalyst. The relatively small range of sulfur concentrations and the short duration of the experiments did not permit the authors to establish the relation of catalyst activity to concentration of poison, and to the time that the catalyst is in work.

The effect of sulfur concentration and partial pressure of hydrogen on the activity and stability of a platinum catalyst in the production of aromatic hydrocarbons was established by Meerboot and co-workers [11]. The authors showed that with a sulfur content of 0.02% in the raw material, and a partial pressure of hydrogen of 12.2 atm, the activity of the catalyst falls rapidly, whereas, at 15.6 atm and the same sulfur content, the catalyst can operate for a long time without substantial change in activity. On the other hand, sulfur at a concentration of 0.03% appreciably suppresses the aromatizing power of the catalyst at 15.6 atm, but increase of the partial pressure of hydrogen to 19 atm results in maintenance of catalyst activity, even if the sulfur concentration is increased to 0.05%. The work of Hettinger and co-workers [12] is concerned with the effect of sulfur on the dehydrocyclizing power of platinized alumina. The authors observed a considerable reduction in the yield of toluene in the dehydrocyclization of heptane containing 0.8% of sulfur at 482° and 13.6 atm of hydrogen. In the investigation [13], a study was made of the effect of sulfur concentration on the rate of deactivation of a platinum catalyst in the aromatization of a gasoline fraction. Sulfur at concentrations of 0.01, 0.07, and 0.1% was present in the raw material, and the rate of fall of activity was almost ten times as great at 0.17% than at 0.01%.

In the present investigation on the poisoning of a platinum catalyst under reforming conditions, we set ourselves the following tasks: 1) to establish the relation of the aromatizing activity of the catalyst to the concentration of thiophene in cyclohexane in its dehydrogenation under reforming conditions; 2) to determine the possibility of regenerating poisoned catalysts.

EXPERIMENTAL

The catalyst was prepared as follows. Aluminum hydroxide was prepared by precipitation from 1 M aluminum nitrate solution with 12% aqueous ammonia. The resulting hydrogel was washed free from nitrate ions, filtered off, and dried at 130-140° for 6-8 hours. The resulting mass was roasted at 500° for 3-4 hours and ground to a powder; the powder was impregnated with chloroplatinic acid solution, dried at 120-130° for 5-6 hours, and molded in a special press into cylindrical tablets, 3 x 4 mm in size. The resulting catalyst, which contained 1% of platinum, was reduced in a stream of electrolytic hydrogen for ten hours at 320-330°.

The cyclohexane for use in the experiments was subjected to chromatography on silica gel to remove traces of benzene, and it was then distilled through a column of 15-plate efficiency. As the catalyst poison we used thiophene. This substance was chosen because of the ease with which it could be detected. The thiophene contents of the mixtures prepared were 0.03, 0.37, 0.53, 0.79, 1.05, 2.10, 2.36, 3.85, 6.24, and 9.33%.

All the experiments on the dehydrogenation of cyclohexane containing various amounts of catalyst poison were carried out in a flow-type apparatus at 450°, under a hydrogen pressure of 20 atm at a space velocity of 2 hour⁻¹ and at a ratio of H₂ : hydrocarbon of 5. Each experiment lasted 20 hours. The activity of the catalyst was determined from the benzene content of the catalyzate, which was determined refractometrically [14]. The results obtained by this method agreed closely with those obtained by the relative dispersion and sulfuric acid methods. In order to observe the variation of catalyst activity with time, catalyzate was removed after definite intervals of time during the whole experiment. The first sample of catalyzate was taken ten minutes after the start of the experiment, and further samples were taken every 30 minutes over a period of 2.5-3 hours. The feed of raw material was then discontinued, a little catalyzate was collected for analysis, and the experiment was continued with removal of the catalyzate every two hours. One part of the catalyst was taken from the reactor and used for x-ray structure analysis, and another part was taken for sulfur estimation.

To trap hydrogen sulfide formed by the decomposition of thiophene, the gas leaving the apparatus was passed successively through several Tishchenko vessels containing a mixture of 10% solutions of sodium acetate and zinc nitrate acidified with acetic acid. In view of the fact that much of the hydrogen sulfide dissolved in the catalyzate, each portion of the latter was shaken with the above-mentioned mixture. As a result, almost all the hydrogen sulfide liberated was precipitated as zinc sulfide, the amount of which was determined iodometrically. In some experiments the gas, purified from hydrogen sulfide, was analyzed in a VTI-2 apparatus. Each portion of the catalyzate was tested for thiophene. When unchanged thiophene was found in the catalyzate, it was extracted as the tetraacetoxymercury derivative [15]. For this purpose, mercuric oxide was dissolved in hot glacial acetic acid, the solution was filtered, and the thiophene-containing catalyzate was boiled with this solution in a water bath for two hours. The mixture was then boiled with water, filtered off on a Buchner funnel, and dried in a drying oven at 120°. It was shown by experiments with artificial mixtures that thiophene is separated quantitatively by this method.

Our experimental results are presented in the table and by the curves of Figures 1-3.

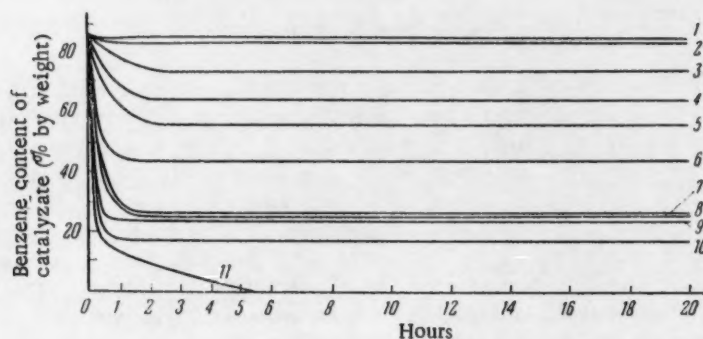


Fig. 1. Change in activity of catalysts with time in the dehydrogenation of cyclohexane containing various amounts of thiophene: 1) 0%; 2) 0.03%; 3) 0.37%; 4) 0.53%; 5) 0.79%; 6) 1.05%; 7) 2.10%; 8) 2.36%; 9) 3.85%; 10) 6.24%; and 11) 9.33% of thiophene.

From the results in the table, we can draw the following main conclusion: In all experiments (except Expt. 11) the aromatizing activity of the catalyzate diminishes only in the first 1-2 hours of work; it then becomes stabilized and is independent of the time of the catalyst in work and, therefore, of the amount of thiophene passed over the catalyst. The reduction in the activity of the catalyst in the first period of its work is determined by the content of poison in the original cyclohexane. Thus, at a thiophene concentration of 0.03%, the activity of the catalyst is almost unchanged. Increase in the thiophene content from 0.37 to 6.24% is accompanied by reduction in catalyst activity from 85.2 to 16.8%; for the complete suppression of its activity more than 9% of thiophene is required.

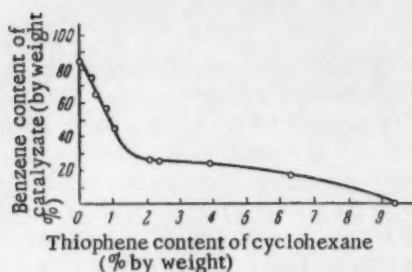


Fig. 2. Relation of aromatizing power of 1% Pt-Al₂O₃ to thiophene content of cyclohexane.

A linear relation between catalyst activity and concentration of poison was observed by Maxted [3], for the poisoning of metal catalysts (Pt, Ni) under the conditions of the liquid-phase hydrogenation of unsaturated compounds, and this relation held right up to complete suppression of the activity of the catalyst. In our experiments, a similar linear relation holds only at low concentrations of thiophene (up to 1%). Further increase in the thiophene content (1-6%) is accompanied by a less marked reduction in catalyst activity.

It has already been stated that during the experiments a check was kept on the thiophene content of the catalysts. It was found that in mixtures containing thiophene in concentrations of up to 1.05%, the latter is completely decomposed to hydrogen sulfide during passage over the catalyst. However, at concentrations of 2.1% and higher, part of the thiophene passes unchanged over the catalyst. Thus, in Expt. 9 (poison concentration 3.85%) 6.5% of the thiophene introduced was isolated from the catalyzate as the tetraacetoxymercury derivative. Elementary analysis showed that after being poisoned, the catalysts contained only a very small amount (less than 0.01%) of sulfur. The question of the form in which this sulfur occurs on the catalyst still remains open. X-ray structure analysis of poisoned catalysts did not reveal the appearance of new phases; there were only the lines corresponding to aluminum oxide and platinum.

It is known from the literature that the poisoning of platinum catalysts working both under conditions of dehydrogenation catalysis (300°, atmospheric pressure) and under more severe conditions (460-480°, 20-40 atm of H₂) by sulfur-containing organic substances is reversible. These results were confirmed in our investigations. Four samples of catalyst which had been poisoned in dehydrogenation of cyclohexane having various thiophene contents were subjected to regeneration. The regeneration of these catalysts was carried out with pure cyclohexane under the same conditions as those of the poisoning process. The curves (Fig. 3) show that all the catalysts were regenerated with recovery of the original level of activity. However, the time required for regeneration was determined by the thiophene concentration used in the poisoning of the catalysts. The content of carbonaceous deposits was approximately the same (0.6-0.7%) in all the poisoned catalysts. The blocking of active centers by carbonaceous deposits appeared to be of secondary importance in the deactivation of the catalysts.

EXPERIMENTAL RESULTS

It follows from the results that the passage of cyclohexane with additions of thiophene over the catalyst is accompanied by a sharp reduction in the activity of the catalyst to a certain level, dependent on the thiophene content of the original cyclohexane, but independent of the duration of the experiment and, therefore, of the amount of thiophene passed (see Fig. 1). On the other hand, passage of pure cyclohexane (instead of its mixture with thiophene) over a poisoned catalyst leads to the recovery of the original activity (see Fig. 3). It is evident that the regeneration of the catalyst occurs during an experiment with mixtures of cyclohexane and thiophene of constant composition. The stationary activity of the catalyst established during an experiment is probably determined by a dynamic equilibrium in which the rate of blocking active centers by decomposition products of thiophene is equal to the rate of regeneration of the active centers.

It is more difficult to explain the presence of unchanged thiophene in the catalyzates (Experiments 9-11) in spite of the fact that in these experiments, the activity of the catalysts toward cyclohexane still remained at a considerable level. It is probable that the partial deactivation of catalysts, both toward the dehydrogenation

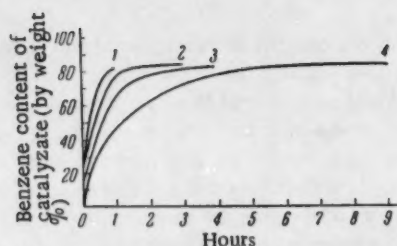


Fig. 3. Regeneration of catalysts poisoned in the dehydrogenation of cyclohexane containing thiophene: 1) 2.36%; 2) 3.85%; 3) 6.24%, and 4) 9.33%. Temperature 450°; P_{H₂} = 20 atm; \bar{v} = 2 hour⁻¹; H₂ : hydrocarbon = 5 : 1.

Change in the Activities of Catalysts in the Dehydrogenation of Cyclohexane Containing Various Amounts of Thiophene
($t = 450^\circ$; $P_{H_2} = 20$ atm; $v = 2$ hour $^{-1}$; H_2 : hydrocarbon = 5 : 1)

Expt.	Thiophene content of cyclohexane (%) by wt.)	Benzene content of catalyzate (%) after						Reduction in aromatizing activity in 20 hours (%) of original)	Qualitative test for thiophene
		10 min	30 min	1 hour	1.5 hours	2 hours	2.5 hours	3 hours	
1	0	86,0	86,0	—	85,8	85,0	84,8	—	—
2	0,03	—	—	—	—	83,7	84,4	—	—
3	0,37	83,2	81,0	80,0	76,0	75,9	73,2	72,2	1,1
4	0,53	82,0	75,2	65,2	63,5	65,2	63,9	64,0	13,1
5	0,79	78,0	68,0	62,0	62,3	56,8	60,2	56,0	23,9
6	1,05	68,4	50,0	45,0	44,5	43,8	44,4	44,5	33,8
7	2,40	59,3	39,6	29,8	25,8	26,3	—	27,7	46,6
8	2,36	59,0	39,2	29,0	25,3	25,8	25,8	25,6	68,9
9	3,85	54,6	25,4	25,0	24,0	25,8	22,2	16,8	69,6
10	6,24	37,5	19,8	14,8	18,4	18,2	—	4,1	71,4
11	9,33	16,4	14,6	12,2	10,5	8,2	—	0	80,3
									100,0
									Positive
									Negative

of cyclohexane and toward the destructive hydrogenation of thiophene, was determined by the fact that both of these reactions occur at the same active centers. In this case, the blocking of active centers by decomposition products of thiophene (probably H_2S) leads to a reduction in the extent of both reactions. It may be supposed that, because of the much greater adsorption of thiophene than that of cyclohexane, simultaneous dehydrogenation of cyclohexane and destructive hydrogenation of thiophene is possible only when the concentration of the latter is very low. Increase in thiophene concentration to 9.33% (Expt. 11) leads to complete deactivation of the catalyst for the dehydrogenation of cyclohexane, i.e., to complete displacement of the latter from the catalyst surface by thiophene or hydrogen sulfide.

The above hypothesis of the blocking of active centers by hydrogen sulfide is in accord with results obtained by us [8] and by Heinemann and co-workers [10] concerning the independence of the rate of deactivation of catalysts on the structure of the sulfur compound. All these compounds are probably decomposed to hydrogen sulfide, and the slowness of the desorption of the latter from the surface of the catalyst results in deactivation not only in the dehydrogenation of cyclohexane, but also in the destructive hydrogenation of the sulfur compounds. From this point of view, the regeneration of catalysts poisoned by sulfur compounds consists in the desorption of hydrogen sulfide from the catalyst surface.

The x-ray structure analysis of the catalysts was carried out in A. M. Rubinshtein's laboratory, and the authors express their thanks for this service.

SUMMARY

1. An investigation was made of the poisoning of a 1% Pt- Al_2O_3 catalyst by thiophene in the dehydrogenation of cyclohexane in a flow system at 450° in presence of hydrogen at 20 atm.

2. When mixtures of cyclohexane and thiophene of constant composition were passed over the catalyst the dehydrogenation activity fell only during the first 1-2 hours, after which, it remained constant and no longer depended on the amount of thiophene passed over the catalyst. The reduction in the activity of the catalyst in the first hours of work is determined by the thiophene content of the original mixture.

3. Poisoned catalysts recover their original activity when pure cyclohexane is passed over them; however, the time required for regeneration is determined by the thiophene concentration of the original mixture used in the poisoning of the catalyst.

4. On the basis of the results obtained in this and our earlier investigations, it is suggested that the deactivation of platinum catalysts is determined by the rate of the desorption of thiophene and hydrogen sulfide which is formed in the decomposition of various sulfur compounds.

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ADDITION OF ALIPHATIC β -NITRO ALCOHOLS TO VINYL ETHERS

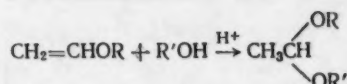
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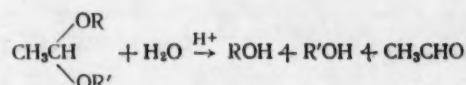
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 2, pp. 307-310, February, 1960

Original article submitted May 22, 1958

Vinyl ethers combine smoothly with alcohols in presence of acid catalysts with formation of the corresponding acetaldehyde acetals [1]:



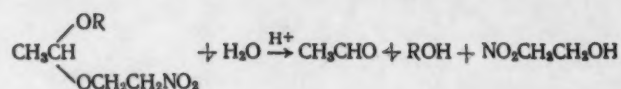
This reaction provides an excellent method of temporarily protecting a hydroxy group in reactions in which the presence of this group is undesirable. The acetals formed are very readily hydrolyzed with dilute sulfuric acid with regeneration of the original alcohol [2]:



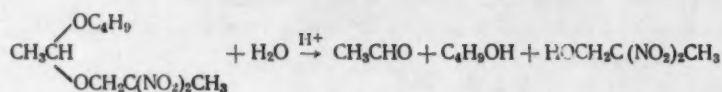
The present paper describes the addition of β -nitro alcohols to ethyl, isopropyl, and butyl vinyl ethers. The reaction goes smoothly in presence of catalytic amounts of hydrogen chloride with evolution of much heat. The nitro alcohols that were caused to add to ethyl vinyl ether were 2-nitroethanol, 2,2,2-trinitroethanol, 2,2-dinitro-1-propanol, 1-nitro-2-propanol, and 3-nitro-2-butanol, and no substantial difference was found in the reaction of the vinyl ether with primary and with secondary alcohols. Both to isopropyl vinyl ether and to butyl vinyl ether addition of primary (2-nitroethanol, 2,2-dinitro-2-propanol) and secondary (1-nitro-2-propanol) alcohols went with equal ease.

The acetals obtained from vinyl ethers and nitro alcohols have some peculiarities in their physical properties which distinguish them from the corresponding acetals which do not contain nitro groups. As would be expected, the introduction of a nitro group greatly raises the density and refractive index of the acetal, and the effect is the greater, the larger the number of nitro groups in the molecule. An examination of the changes in density and refractive index in the series of acetals $\text{CH}_3\text{CH}(\text{OR})(\text{OC}_2\text{H}_5)$ or $\text{CH}_3\text{CH}(\text{OR})(\text{OC}_3\text{H}_7)$, in which $\text{R} = \text{C}_2\text{H}_5$, C_3H_7 , or C_4H_9 [1] leads to the following conclusions: In the series $\text{R} = \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_7 \rightarrow \text{C}_4\text{H}_9$, the refractive index gradually rises, but on replacement of C_2H_5 by C_3H_7 (or $i\text{-C}_3\text{H}_7$) the density falls, though it rises again when $\text{R} = \text{C}_4\text{H}_9$ and becomes even greater than for the acetal in which $\text{R} = \text{C}_2\text{H}_5$. For the acetals of the series $\text{CH}_3\text{CH}(\text{OR})\text{OCH}(\text{CH}_3)\text{CH}_2\text{NO}_2$, and $\text{CH}_3\text{CH}(\text{OR})\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3$, the changes in density and refractive index follow a different pattern. In all these series, as we pass from $\text{R} = \text{C}_2\text{H}_5$ to $\text{R} = i\text{-C}_3\text{H}_7$ the refractive index diminishes by 0.0070-0.0087, whereas for the acetals in which $\text{R} = \text{C}_4\text{H}_9$ the refractive index increases by 0.0032-0.0056; in all cases the greatest change is found for acetals prepared from 2-nitroethanol ($-\text{OCH}_2\text{CH}_2\text{NO}_2$) and the least for acetals prepared from 2,2-dinitro-1-propanol [$-\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3$]. The densities of the acetals of all the

above-mentioned series fall regularly in the order $R = C_2H_5 > i-C_3H_7 > C_4H_9$, and the greatest change occurs as we pass from $R = C_2H_5$ to $R = i-C_3H_7$ (table). The acetals synthesized were readily hydrolyzed by 5% sulfuric acid which was shown in the case of the products of addition of 2-nitroethanol to ethyl, isopropyl, and butyl vinyl ether; also in the case of the addition product from 2,2-dinitro-1-propanol and butyl vinyl ether:



in which $R = C_2H_5, i-C_3H_7, n-C_4H_9$.



Refractive Indices and Densities of Acetals Obtained

Acetal	n_D^{20}	d_4^{20}	MR	
			found	calculated
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_2\text{H}_5 \\ \diagdown \text{OCH}_2\text{CH}_2\text{NO}_2 \end{array}$	1,4331	1,0964	38,65	38,81
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_3\text{H}_7, i \\ \diagdown \text{OCH}_2\text{CH}_2\text{NO}_2 \end{array}$	1,4244	1,0458	43,22	43,42
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_4\text{H}_9, n \\ \diagdown \text{OCH}_2\text{CH}_2\text{NO}_2 \end{array}$	1,4300	1,0284	47,98	48,04
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_2\text{H}_5 \\ \diagdown \text{OCH}(\text{CH}_3)\text{CH}_2\text{NO}_2 \end{array}$	1,4332	1,0694	43,03	43,42
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_3\text{H}_7, i \\ \diagdown \text{OCH}(\text{CH}_3)\text{CH}_2\text{NO}_2 \end{array}$	1,4261	1,0227	47,86	48,04
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_4\text{H}_9, n \\ \diagdown \text{OCH}(\text{CH}_3)\text{CH}_2\text{NO}_2 \end{array}$	1,4306	1,0060	52,70	52,66
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_2\text{H}_5 \\ \diagdown \text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3 \end{array}$	1,4405	1,2103	48,39	49,04
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_3\text{H}_7, i \\ \diagdown \text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3 \end{array}$	1,4335	1,1526	53,27	53,66
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_4\text{H}_9, n \\ \diagdown \text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3 \end{array}$	1,4367	1,1196	58,46	58,27
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_2\text{H}_5 \\ \diagdown \text{OCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NO}_2 \end{array}$	1,4270	1,0300	47,61	48,04
$\text{CH}_3\text{CH} \begin{array}{l} \diagup \text{OC}_2\text{H}_5 \\ \diagdown \text{OCH}_2\text{C}(\text{NO}_2)_3 \end{array}$	1,4435	1,2943	51,88	49,03

EXPERIMENTAL

Reaction of β -Nitro Alcohols with Vinyl Ethers

The nitro alcohol (in the case of trinitroethanol and 2,2-dinitro-1-propanol a solution of the alcohol in an equal volume of dry ether was taken) and 0.5 ml of dry ether saturated with dry hydrogen chloride were introduced into a three-necked flask fitted with a glycerol-sealed mechanical stirrer, reflux condenser, and dropping funnel. The mixture was stirred while the vinyl ether was added from the dropping funnel, and by cooling and control of the rate of addition of the vinyl ether, the temperature of the mixture was kept below 25-30°. The mixture was allowed to stand until the next day and was then fractionated.

2-Nitroethanol. a) From 9.1 g of nitroethanol and 15 ml of ethyl vinyl ether, we obtained 10.6 g (65%) of acetaldehyde ethyl 2-nitroethyl acetal; b.p. 85-87° (4 mm); n_D^{20} 1.4331; d_4^{20} 1.0964; found MR 38.65; calculated MR 38.81. Found: C 44.10; 43.88; H 8.10; 7.94; N 8.77; 8.68%. $C_6H_{13}NO_4$. Calculated: C 44.17; H 8.00; N 8.59%.

b) From 9.1 g (55%) of acetaldehyde isopropyl 2-nitroethyl acetal; b.p. 83-85° (3 mm); n_D^{20} 1.4244; d_4^{20} 1.0458; found MR 43.22; calculated MR 43.42; Found: C 47.41; 47.33; H 8.44; 8.45%. $C_7H_{15}NO_4$. Calculated: C 47.46; H 8.47%.

c) From 9.1 g of nitroethanol and 20 ml of butyl vinyl ether, we obtained 11.1 g (59%) of acetaldehyde butyl 2-nitroethyl acetal; b.p. 98-101° (4 mm); n_D^{20} 1.4300; d_4^{20} 1.0284; found MR 47.98; calculated MR 48.04. Found: C 49.90; 49.88; H 8.80; 8.82%. $C_8H_{17}NO_4$. Calculated: C 50.26; H 8.90%.

1-Nitro-2-propanol. a) From 10.5 g of 1-nitro-2-propanol and 20 ml of ethyl ether, we obtained 11.5 g (65%) of acetaldehyde ethyl 1-methyl-2-nitroethyl acetal; b.p. 72-74° (3 mm); n_D^{20} 1.4332; d_4^{20} 1.0694; found MR 43.03; calculated MR 43.42. Found: C 47.44; 47.31; H 8.52; 8.44%. $C_7H_{15}NO_4$. Calculated: C 47.46%; H 8.47%.

b) From 5.5 g of 1-nitro-2-propanol and 12 ml of isopropyl vinyl ether, we obtained 5.6 g (50%) of acetaldehyde isopropyl 1-methyl-1-2-nitroethyl acetal; b.p. 75-77° (3 mm); n_D^{20} 1.4261; d_4^{20} 1.0227; found MR 47.86; calculated MR 48.04. Found: C 50.06; 50.12; H 8.77; 8.85%. $C_8H_{17}NO_4$. Calculated: C 50.26; H 8.90%.

c) From 5.5 g of 1-nitro-2-propanol and 15 ml of butyl vinyl ether, we obtained 7.7 g (75%) of acetaldehyde butyl 1-methyl-2-nitroethyl acetal; b.p. 92-94° (3 mm); n_D^{20} 1.4306; d_4^{20} 1.0060; found MR 52.70; calculated MR 52.66. Found: C 52.45; 52.61; H 9.26; 9.21%. $C_9H_{19}NO_4$. Calculated: C 52.68; H 9.27%.

2,2-Dinitro-1-propanol. a) From 7.5 g of 2,2-dinitro-1-propanol and 12 ml of ethyl vinyl ether, we obtained 9.2 g (89%) of acetaldehyde 2,2-dinitropropyl ethyl acetal; b.p. 96-99° (4 mm); n_D^{20} 1.4405; d_4^{20} 1.2103; found MR 48.39; calculated MR 49.04. Found: C 37.62; 37.53; H 6.21; 6.48%. $C_7H_{14}N_2O_6$. Calculated: C 37.83; H 6.31%.

b) From 7.5 g of 2,2-dinitro-1-propanol and 15 ml of isopropyl vinyl ether, we obtained 7.8 g (66%) of acetaldehyde 2,2-dinitropropyl isopropyl acetal; b.p. 99-102° (4 mm); n_D^{20} 1.4335; d_4^{20} 1.1526; found MR 53.27; calculated MR 53.66. Found: C 40.22; 40.37; H 6.96; 6.65%. $C_8H_{15}N_2O_6$. Calculated: C 40.68; H 6.78%.

c) From 7.5 g of 2,2-dinitro-1-propanol and 15 ml of butyl vinyl ether, we obtained 8.7 g (70%) of acetaldehyde butyl 2,2-dinitropropyl acetal; b.p. 116-120° (5 mm); n_D^{20} 1.4367; d_4^{20} 1.1196; found MR 58.46; calculated MR 58.27. Found: C 43.57; 43.54; H 7.33; 7.22%. $C_9H_{18}N_2O_6$. Calculated: C 43.20; H 7.20%.

3-Nitro-2-butanol. From 6.5 g of 3-nitro-2-butanol and 10 ml of ethyl vinyl ether, we obtained 7.9 g (83%) of acetaldehyde ethyl 1-methyl-2-nitropropyl acetal; b.p. 73-75° (3 mm); n_D^{20} 1.4270; d_4^{20} 1.0300; found MR 47.61; calculated MR 48.04. Found: C 50.18; 49.93; H 8.85; 8.80%. $C_8H_{17}NO_4$. Calculated: C 50.26; H 8.90%.

2,2,2-Trinitroethanol. From 9 g of trinitroethanol and 20 ml of ethyl vinyl ether, we obtained 8.4 g (67%) of acetaldehyde ethyl 2,2,2-trinitroethyl acetal; b.p. 84-86° (3 mm); n_D^{20} 1.4435; d_4^{20} 1.2943; found MR 51.88; calculated MR 49.03. Found: C 27.82; 27.70; H 4.45; 4.65; N 16.33; 16.23%. $C_6H_{11}N_3O_8$. Calculated: C 28.46; H 4.35; N 16.60%.

Hydrolysis of Acetals

Acetaldehyde Ethyl 2-Nitroethyl Acetal. A mixture of 8.4 g of the acetal and 100 ml of 5% sulfuric acid was heated with stirring in a water bath for two hours. The cooled solution was saturated with ammonium sulfate

and extracted repeatedly with ether. The ether solution was dried with sodium sulfate and fractionated. We obtained 3.4 g of 2-nitroethanol, b.p. 74-78° (5 mm) and n_D^{20} 1.4406.

Acetaldehyde Isopropyl 2-Nitroethyl Acetal. In an analogous way 5.4 g of the acetal was hydrolyzed with 50 ml of 5% sulfuric acid. We obtained 2.2 g of nitroethanol.

Acetaldehyde Butyl 2-Nitroethyl Acetal. The acetal (3.5 g) was hydrolyzed with 5% sulfuric acid (100 ml) in the way described above. We obtained 1.1 g of nitroethanol.

Acetaldehyde Butyl 2,2-Dinitropropyl Acetal. The acetal (5 g) was heated for two hours at 100° with 50 ml of 5% sulfuric acid, and the product was treated in the usual way. The ether solution was dried, and low-boiling substances were distilled off. When cool, the residue solidified. We obtained 2.3 g of 2,2-dinitro-1-propanol.

SUMMARY

1. The addition of various aliphatic β -nitro alcohols to ethyl, isopropyl, and butyl vinyl ethers has been carried out for the first time, and the resulting acetals have been characterized.
2. Some of the acetals synthesized were hydrolyzed with regeneration of the original nitro alcohol.

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REACTIONS OF FREE RADICALS IN SOLUTIONS

COMMUNICATION 15. MECHANISM OF THE DEGRADATION OF POLYMERS UNDER THE ACTION OF FREE RADICALS

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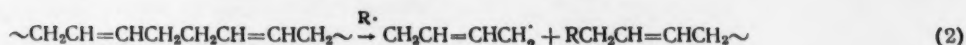
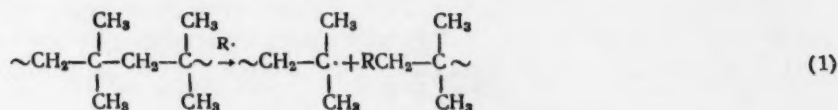
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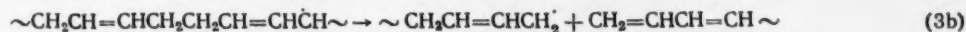
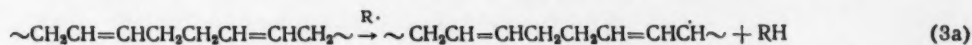
In a series of papers published previously [1-3], data were presented which showed that various free radicals initiate the degradation of saturated and unsaturated polymers. In these papers, two possible mechanisms of this reaction were suggested:

1. Direct attack of C-C bonds of the skeleton by free radicals



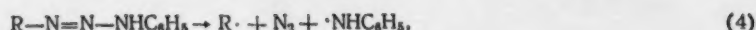
The probabilities of such acts are determined by the fact that in the chain transfer free radicals of greater stability are formed: tertiary in the case of polyisobutylene and radicals of the allyl type in the case of polybutadiene and polyisoprene.

2. Removal of an H-atom by the free radical with subsequent breakdown of the polymeric radical formed



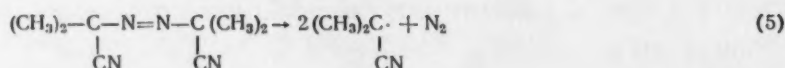
The facts presented in the present paper enable us to conclude that the second scheme is correct, i.e., the process is associated with the removal of an H-atom as the primary act.

The relation of the efficiency of the degradation process to the nature of the initiating radical (for free alkyl radicals) was studied most fully for the case of polyisobutylene by Romanov et al [2]. As sources of free radicals they used triazenes, which decompose when heated in solution in accordance with the equation:

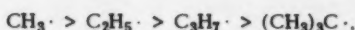


in which $R = CH_3\cdot$, $C_2H_5\cdot$, $n-C_3H_7\cdot$, $i-C_3H_7\cdot$, and $(CH_3)_3C\cdot$

It was shown that heating of a solution of polyisobutylene in presence of methyl-, ethyl-, and propyl-phenyltriazenes causes a lowering of viscosity (Fig. 1). The strongest effect is shown by free methyl radicals. As absence of viscosity lowering was noted for the radicals $(CH_3)_2\dot{C}$ and $(CH_3)_2\dot{C}-CN$. For the generation of the latter, 2,2'-azobis [2-methylpropionitrile] was used:



It follows from these results that the activities of the free radicals studied in the reaction under consideration fall in the order:



which corresponds completely with the variation of the activities of the same free radicals for the removal of an H atom [4]. It was of interest to determine the possibility of effecting degradation under the action of free radicals in which the reaction center was a sulfur or nitrogen atom. For this purpose, we studied the change in the viscosity of polyisobutylene solutions under the conditions for the thermal decomposition of such sources of free radicals as bis(dimethylthiocarbamoyl) disulfide, 2,2-dithio-

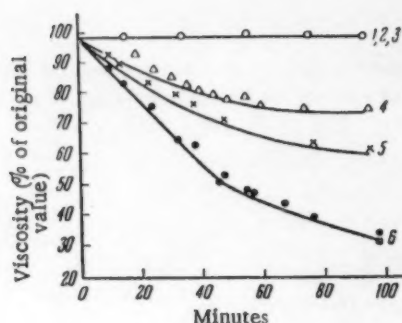
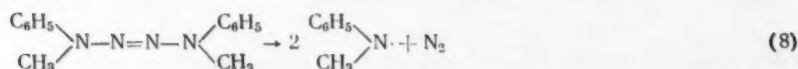
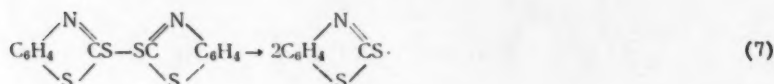
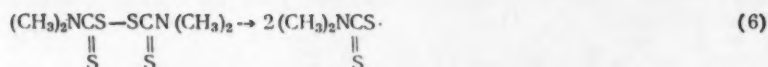


Fig. 1. Degradation of polyisobutylene in ethylbenzene solution in presence of sources of free alkyl radicals at 110°: 1) Without triazene; 2) t-butylphenyltriazene; 3) 2,2'-azobis [2-methylpropionitrile]; 4) phenylpropyltriazene; 5) ethylphenyltriazene; 6) methylphenyltriazene.

bisbenzothiazole, and dimethyldiphenyltetrazene. The decompositions of these compounds in solution proceed according to the equations:



We have shown that heating of a solution of polyisobutylene in ethylbenzene with any of the compounds listed leads to an appreciable lowering of viscosity (Fig. 2). The comparatively small quantitative effect may be associated with the low activity of free radicals formed by Equations (6)-(8) in the reaction of hydrogen removal.

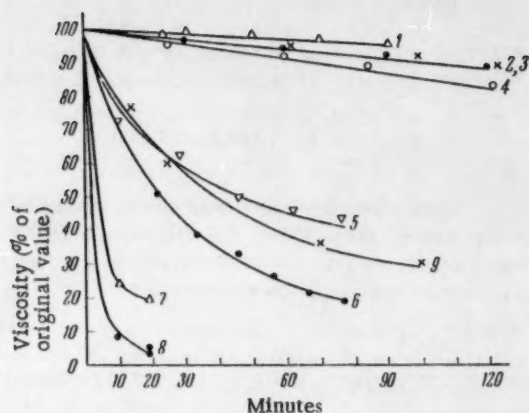


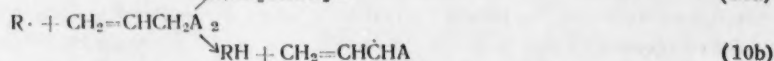
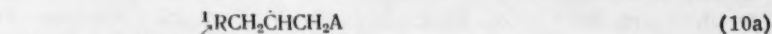
Fig. 2. Degradation of polyisobutylene in ethylbenzene solution in presence of sources of free heteroradicals: 1) Without initiator, 130°; 2) 2,2-dithiobisbenzothiazole, 130°; 3) dimethyldiphenyltetrazene, 130°; 4) bis (dimethylthiocarbamoyl) disulfide, 130°; 5) cumene hydroperoxide + ferric naphthenate (10 moles % on hydroperoxide), 110°; 6) benzoyl peroxide, 90°; 7) cumene hydroperoxide + cobalt naphthenate (0.5 mole % on hydroperoxide), 110°.

It must be pointed out that, because of the relatively low concentration of polymer in the systems studied the main reaction of the free radicals is that with the solvent. As a result, there arise new free radicals, which, when ethylbenzene is used as solvent, must be radicals of the benzyl type:



It is known that benzyl radicals do not take part in H-atom removal [4, 5]. As we have already pointed out, free radicals of low activity in the reaction of H-atom removal do not lower the viscosity of polyisobutylene.

For the determination of the mechanism of the degradation process, it was of great interest to study the readiness with which the process occurred in presence of free radicals with a reaction center on an oxygen atom. It follows from the literature that radicals of this type (hydroxyls, alkoxyls, and acyls) possess particularly high activity in the H-atom removal reaction [6-8]. The higher activity of such radicals in the reaction under consideration, as compared with free hydrocarbon radicals, is illustrated by the character of their interaction with unsaturated compounds. Thus, of the two competing reactions with α -olefins,



it is mainly the first that occurs with hydrocarbon radicals [9]. On the other hand, radicals of the $RO\cdot$ type react almost exclusively by removal of a hydrogen from α -olefins [6, 10]. From this it would be expected that, if degradation proceeds by the hydrogen-removal scheme, the readiness with which the process occurs will be greater for $RO\cdot$ radicals than for hydrocarbon radicals. This view was confirmed for benzoyl peroxide, whose decomposition in solution is accompanied by the formation of $C_6H_5COO\cdot$ radicals, and cumene hydroperoxide, which forms radicals of $RO\cdot$ and $RO_2\cdot$ types, when it decomposes in presence of salts of metals of variable valence [10]. We have shown that under comparable conditions, benzoyl peroxide produces a much more notable effect than methylphenyltriazene. Similar results were obtained with cumene hydroperoxide, the experiments with which were carried out in presence of a little cobalt or iron naphthenate (see Fig. 2). It was shown previously [1] that oxidation-reduction systems whose action is associated with the formation of free $HO\cdot$ and $HO_2\cdot$ radicals (systems in which oxygen participates) are more effective in the degradation of polymers. The mechanism of cleavage of a C-C bond, which we have considered, is in accord with this fact.

The direct connection between reactions of H-atom removal and of C-C bond cleavage becomes particularly obvious when we examine the results obtained in a study of the effect of ferric naphthenate on polyisobutylene. We showed that heating of polyisobutylene swollen in benzene in presence of ferric naphthenate leads to an appreciable degradation effect which increases with increase in the naphthenate concentration (Fig. 3).

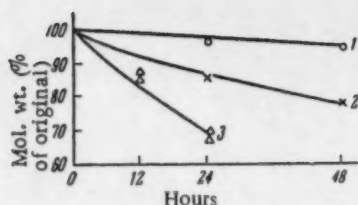


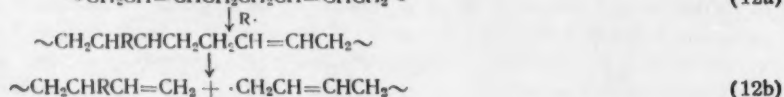
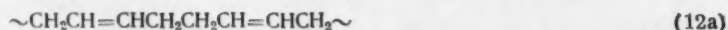
Fig. 3. Degradation of polyisobutylene in presence of ferric naphthenate: 1) in absence of naphthenate; 2) 5 moles % (on polymer) of ferric naphthenate; 3) 20 moles % (on polymer) of ferric naphthenate.

It was shown previously that salts of metals in a higher valence state (ferric, chromic) bring about the dehydrogenation of hydrocarbons and polymer chains at high temperatures [11]. When the reactions are carried out in a medium of polymerizing hydrocarbon, e.g., isoprene, dehydrogenation with formation of free radicals

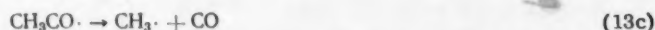
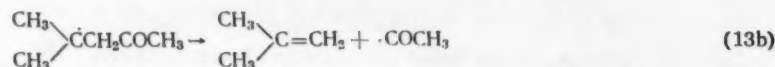
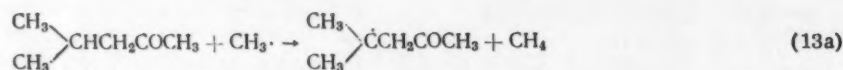


brings about polymerization at only 100°. The degradation of polyisobutylene, which is observed in presence of ferric naphthenate, also appears to pass through the stage of dehydrogenation. Here, the cleavage of the C-C bond must be regarded as a secondary act.

It is noteworthy that free $(\text{CH}_3)_2\dot{\text{C}}\text{-CN}$ radicals, which have low activity for H atom removal [9] and do not bring about the degradation of polyisobutylene, bring about the degradation of natural rubber [3]. This may be explained by the fact that in the case of unsaturated polymers, apart from the H-atom removal reaction, there is the possibility of reaction between initiating free radicals and double bonds. Such acts, which occur to a considerable extent with $(\text{CH}_3)_2\dot{\text{C}}\text{-CN}$ radicals [9], also lead to the formation of polymeric radicals that are capable of further breakdown with rupture of a C-C bond:



The facts presented in the present paper permit us to establish a direct link between the activity of free radicals for H-atom removal and their effectiveness in the initiation of the degradation of polymers. The greatest effect is produced by just those radicals which are particularly reactive in the cleavage of a C-H bond. These results, together with the possibility that we have established of degrading polyisobutylene under the action of a dehydrogenating agent (ferric naphthenate), lead us to the conclusion that the primary act bringing about the degradation of polymers initiated by free radicals is the removal of an H-atom from the polymer chain. The probability of such a mechanism is confirmed also by recently published data on the reaction of a free methyl radical with 4-methyl-2-pentanone [12]. As the investigation cited shows, in this reaction in the gas phase at 150°, methane and other products are accompanied by equivalent amounts of isobutene and carbon monoxide. The authors proposed a scheme according to which the formation of the final products was the result of successive cleavages of C-H and C-C bonds:



EXPERIMENTAL

The polyisobutylene solutions were prepared in Schlenk's apparatus under conditions which excluded the admission of air into the system. Most of the experiments were carried out in ampoule-viscometers, which were filled in an atmosphere of oxygen-free nitrogen. After being filled, the ampoules were sealed. The course of the process was characterized by the change in the time for the flow of a definite volume of polymer solution. In the study of the degradation of polyisobutylene under the action of ferric naphthenate, the necessary amount of a benzene solution of the naphthenate was added (in a countercurrent of nitrogen) to a weighed amount of polyisobutylene in the ampoule. The sealed ampoules were kept for one day at room temperature to ensure uniform distribution of the naphthenate in the polymer, and were then placed in a thermostat at 120°. When the heating was complete, the polyisobutylene was repeatedly precipitated from toluene solution with alcohol and was dried in a vacuum to constant weight. The molecular weight of the polyisobutylene was determined viscometrically in toluene solution.

In the degradation experiments, the concentration of polymer in solution was 3.5% by weight, the concentration of benzoyl peroxide was 0.45% by weight, and the other initiators were taken in amounts equivalent to that of benzoyl peroxide. In experiments in presence of cumene hydroperoxide and cobalt naphthenate, the concentration of the hydroperoxide was double that of benzoyl peroxide. This was necessary because two free radicals are formed per molecule of initiator in the thermal decomposition of benzoyl peroxide, whereas only one free radical is formed in the decomposition of the hydroperoxide in presence of a heavy metal salt.

Starting Materials. Polyisobutylene was reprecipitated from toluene solution with methanol and was dried to constant weight. The disulfides, benzoyl peroxide, and cumene hydroperoxide, preparations of which were already available, were purified. The triazenes were synthesized by Dimrot's method [13] from alkylmagnesium halides and phenyl azide. Dimethyldiphenyltetrazene was prepared by the oxidation of unsymmetrical methylphenylhydrazine with mercuric oxide [14].

SUMMARY

1. The greatest effect is produced in the degradation of polymers by free radicals that are particularly active in H-atom removal reactions.
2. The degradation of polymers under the action of free radicals is probably due to successive acts of a) removal of a hydrogen atom from the polymer chain, and b) spontaneous breakdown at a C-C bond of the polymeric radical formed in the first act.

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COMPONENTS OF THE CATALYST IN THE VAPOR-PHASE SYNTHESIS OF VINYL ESTERS

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Several investigations of recent years have been devoted to matters relating to the synthesis of vinyl acetate from acetylene and acetic acid. The conditions for the preparation of vinyl esters under pressure in presence of a copper catalyst [1] and the kinetics of the formation of vinyl acetate in a static system [2] have been studied. Some of our previous communications [3-6] were devoted to the vapor-phase heterogeneous catalytic synthesis of vinyl acetate and other vinyl esters, which made it possible to obtain high yields in this reaction. In these investigations a zinc carboxylate supported by activated charcoal was used as catalyst. The synthesis was carried out in the vapor phase at atmospheric pressure. The results on the efficiency of the catalyst showed that the combination of zinc salt and carrier was of primary importance. Our experiments showed that, taken separately, zinc acetate and activated charcoal were of low catalytic activity. In accordance with these results, in assessing the significance of activated charcoal and zinc salt, we may suppose that the charcoal takes part in the general cycle of the process under consideration as a sorbent that brings about adsorption and, to an extent depending on the structure of the charcoal and the vapor pressures of the reactants, capillary condensation with creation of the necessary dispersity of the zinc salt catalyst. No light has yet been thrown on the part played by the separate components of the catalytically active zinc salt (its anionic and cationic parts).

In the few patents published on the preparation of vinyl esters and ethers from acetylene by a heterogeneous method without use of pressure, in addition to zinc salts potassium, mercury, magnesium, barium, silver, nickel, and iron salts [7, 8], alkali metal oxides, and soda-lime [9] are mentioned. Since Kucherov's work [10, 11], mercury compounds have acquired special significance as catalysts in addition reactions with acetylene; they are now used for the hydration of acetylene and the synthesis of vinyl acetate in the liquid phase [12]. A thorough study has been made of the quasicomplex character of the products of the addition of a mercury salt to acetylene [13, 14]. Mercuric chloride, deposited together with barium chloride on charcoal, is used for the vapor-phase synthesis of vinyl chloride from acetylene [15].

In examining the desirability of using a particular compound as a catalyst, we must, of course, take account of the extent to which side processes may develop: the polymerization of acetylene, its autodecomposition, its hydration, etc. As we have already stated [6], all the existing experimental material indicates that it is desirable to regard the mechanism of the reactions of acetylene from the point of view of dual reactivity: activation, in various degrees depending on the catalyst present, a) at a C-H bond or b) at the triple bond. It must be here remembered that, in accordance with the composition of the original catalyst, the intermediate complex of organometallic compound will react with the reaction medium preferentially in one of these two directions.

Examining various reactions of acetylene from this point of view, we may note that alkali metal, copper, and nickel salts increase the activation of a carbon-hydrogen bond to a much greater extent than compounds of Group II elements, zinc and mercury. Copper, and also iron, cobalt, and some other Group VIII metals, is unlike

mercury in showing considerable activity at high temperatures and intensifying not only the polymerization of acetylene, but also its autodecomposition into carbon and hydrogen [16, 17]. Some known reactions of acetylene are undoubtedly associated with this mechanism of activation, e.g., the formation of 1-buten-3-yne [18] and the reaction with aldehydes [19]. However, under certain conditions, compounds of these elements used as catalysts enable us to direct processes in the direction of addition, i.e., are fairly effective in activating the π -bond. Examples are the formation of acrylonitrile [15], the Favorskii-Shostakovskii reaction [20], and the preparation of vinyl esters in presence of copper acetylide deposited on fireclay [1]. As Petrov has shown [21], in additions to acetylene an ionic mechanism may be superimposed on a radical mechanism.

Existing data suggest that it is desirable, in the first place, to study the neighbors of zinc and mercury in Group II of the periodic system as catalysts in the vapor-phase preparation of vinyl esters. In the present paper, we report results of experiments with magnesium and cadmium catalysts; their study, while permitting an approach to a generalization of information on the catalytic effects of Group II elements, is of interest because of the difference in volatility between the salts. When the given reaction is carried out in the gas phase, cadmium compounds, which are usually more volatile than zinc compounds, should have a more marked catalytic effect. Experiments showed, however, that cadmium and zinc salts are very similar in activity. In order to study the effect of change of anion, zinc acetate, benzoate, sulfate, and chloride were compared.

EXPERIMENTAL

The main apparatus and the procedure in the heterogeneous catalytic syntheses were similar to those used previously [3, 4]. Checks were made on the process by taking test samples from the gas stream after passage over the catalyst: The contents of free acid and ester were determined. The temperatures in the catalysis tube were checked with two thermocouples: at the point at which the reaction mixture came in contact with the catalyst, and in the middle of the length of the catalyst layer. The diameter of the reaction tube was 18 mm. Acetylene from a cylinder was purified from acetone vapor, passed through geratol columns, washed with caustic alkali solution, and dried. The rate of passage of acetylene, which was usually 10 liters/hour, was checked with a rheometer. In the preparation of the catalyst, magnesium or cadmium acetate, or zinc benzoate, sulfate, phosphate, or chloride was deposited on AG activated charcoal.

The time spent by the reactants in the catalyst zone, calculated with due consideration of the porosity of the catalyst, i.e., from the values of bulk and true density, was about 3.5 seconds for the cadmium salt and about 6 seconds for magnesium acetate. There were about 20 molecules of acetylene per molecule of acid. The results of the experiments are given in Fig. 1. Curves 1, 2, and 3 refer to cadmium acetate catalysts, and the broken lines (curves 1', 2', and 3') to the corresponding zinc acetate catalysts containing, respectively, equimolecular amounts of the salt. With respect to the concentration of salt on the carrier, Curve 3' corresponds approximately to Curve 4 for magnesium acetate, but in the last case the time of contact with the catalyst was increased because of the lower activity of the magnesium salt.

Fig. 1 shows that catalysts containing zinc and cadmium salts are extremely close in activity, but for the less active magnesium catalyst, the temperature range for the reaction was considerably displaced toward higher temperatures.

The experiments with zinc salts of various acids (benzoic, phosphoric, sulfuric, and hydrochloric) as catalysts were carried out under conditions similar to those stated above. The results are given in Fig. 2. In the experiments with zinc benzoate and sulfate (curves 1 and 2), the time of contact was 3.5 seconds. For comparison, we give the corresponding data (Curves 1' and 2') for zinc acetate catalysts. Curve 3 for zinc phosphate (contact time about 7 seconds), may be compared with Curve 3'. The conditions in experiments with zinc chloride were similar.

Fig. 2 shows that change in the anionic part of the catalyst led to some (in certain cases small) lowering of catalyst activity. As compared with zinc benzoate, zinc salts of mineral acids are more marked in their effects on the activity of the catalyst. Thus, for a zinc chloride catalyst the temperature range was about 30-40° higher than for zinc acetate. The salts under consideration may be placed in order of diminishing activity as follows: acetate-benzoate-chloride-sulfate-phosphate.

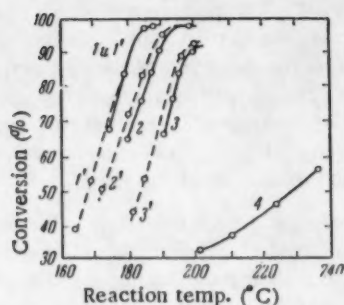


Fig. 1. Catalytic activity of cadmium, magnesium, and zinc acetates: 1) 27% cadmium acetate; 1') 21% zinc acetate; 2) 18% cadmium acetate; 2') 14.3% zinc acetate; 3) 10.3% cadmium acetate; 3') 8% zinc acetate; 4) 11.4% magnesium salt.

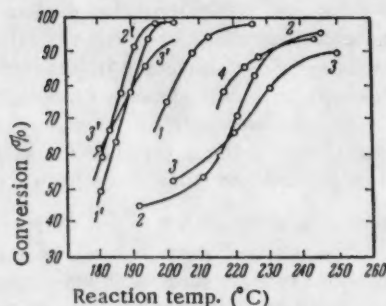


Fig. 2. Comparison of catalytic activities of some zinc salts: 1) 15% zinc benzoate on AG2 charcoal; 2) 10% zinc sulfate on AG2 charcoal; 3) 6.3% zinc phosphate on AG3 charcoal; 4) 7.1% zinc chloride on AG3 charcoal; 1') 9.3% zinc acetate on AG2 charcoal; 2') 12% zinc acetate on AG2 charcoal; 3') 10% zinc acetate on AG3 charcoal.

To find out whether acetic acid vapor reacts with the catalyst with partial replacement of the anion by acetate, prolonged experiments were carried out on the reaction between acetylene and acetic acid in the presence of a zinc benzoate catalyst. As the table shows, during the experiment the activity of the catalyst gradually rose, indicating gradual formation of zinc acetate in the catalyst.

Duration of process (hours)	Conversion (%)
12	76
19	78
22	81

In another experiment carried out under conditions similar to those used for the synthesis of vinyl benzoate [5], benzoic acid vapor was passed over a zinc acetate catalyst containing 19.3% of the salt. In the fractionation of the catalyzed, as well as vinyl benzoate, we obtained a little vinyl acetate. The results of these experiments leave no doubt about the occurrence of chemical reaction between the acidic reactant and the catalyst.

From the results, we may conclude that compounds of Group II elements (zinc, cadmium, and to a less extent magnesium), activate acetylene mainly at the triple bond. As already stated, the catalytic activity of mercury salts [10-14], and also barium salts [15], in addition reactions of acetylene is well known. Taking account of the published experimental data cited above, we must acknowledge that activation at a C-H bond, which favors the occurrence of ethynylation, autodecomposition, formation of cuprene, etc., is much less characteristic for salts of Group II elements than for those of copper and Group VIII elements. Thus, most of the Group II elements are analogous with respect to the catalytic action of their compounds in the reactions of acetylene.

From the results presented in Figures 1 and 2, we may conclude also that the reaction between acetylene and the acid proceeds on the catalyst surface, and not in the bulk (vapor) phase. In the latter case the catalytic activities of various salts would depend to a considerable extent on the vapor pressure of the salt and would rise in the order zinc-cadmium-mercury. However, equimolecular amounts of zinc and cadmium acetates were found to be extremely close in effectiveness. Zinc salts of inorganic acids require the use of higher temperatures. Also, the high conversion of acetic acid under these conditions again indicates the small effect of the volatility of the salt on the effectiveness of the catalyst in the given reaction.

The results are in accord with the low activity which, as already stated, we have found in zinc acetate and activated charcoal used separately as catalysts. The use of them together, however, results in very much increased activity. Hence, the distribution of the catalytically active salt in a thin surface layer and the occurrence of the reaction at the surface of the catalyst determine most of the catalytic effect.

The results show that change in the cation of the salt can have a greater effect on catalytic activity than change in the anion: The cation determines the magnitude, though also the character of the activation of the acetylene molecule. The anion mainly has another function—one of chemisorption. It may be supposed that the adsorption of acetic acid vapor, which is evidently more marked when an acetate is used, passes into chemisorption, and further into a chemical union with acetylene, which has already been coordinately bound to the catalyst salt. The question of the possible specific action of charcoal and its comparison with other carriers requires further study.

SUMMARY

1. From a study of the catalytic activities of cadmium and magnesium acetates and various zinc salts in the heterogeneous catalytic vapor-phase synthesis of vinyl acetate, the effect of change in the cation and the anion of the salt on the reaction of the acetic acid was established.

2. A discussion is given of the effect of compounds of Group II elements in tending to promote reactivity of one given type in acetylene.

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STERIC HINDRANCE AND MOLECULAR CONFORMATION

COMMUNICATION 2. X-RAY INVESTIGATION OF POLYHALOBENZENES AND THEIR DERIVATIVES

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This paper presents the results of a preliminary x-ray investigation of polyhalobenzenes and their derivatives (15 compounds in all) which we had at our disposal; the investigation had the object of obtaining a general crystallochemical characterization of these substances, to select the most promising of them from the point of view of complete structural analysis, and to determine the conformations of their molecules. These conformations may be found to be unusual because of the presence of substantial steric hindrance [1].

EXPERIMENTAL

Goniometric measurements were made on all the crystals studied by means of a Chapskii two-circle goniometer, and stereographic projections were constructed. However, as a result of the poorness of crystal-face development, in particular the absence of end-faces, which is characteristic of the crystals of organic compounds, in most cases, the results of goniometric measurements did not permit unequivocal conclusions to be drawn concerning the symmetry of the crystals. Almost all the crystals studied were tested for the occurrence of a piezoelectric effect. The results of this test were useful in the selection of the space group.

In all cases, we determined the parameters of the unit cells, the space groups, and the number of molecules in a cell, and we calculated also the volumes of the cells and the packing coefficients. The x-ray investigation was carried out by the oscillation method, by the Laue method, by reciprocal lattice photography, and with the Weissenberg x-ray goniometer. The x-ray photographs obtained by the oscillation method were taken with an RKOP camera and were used for the determination of the cell repeats. The x-ray goniometric methods, mainly the method of reciprocal lattice photographs, were used for determining the extinctions, i.e., the space groups, the intensities of reflections for some of the specimens, and also cell repeats and monoclinic angles for needle-like crystals, where the oscillation method is convenient only for the determination of the repeat in the direction of greatest elongation. The Laue method was of value for orienting poorly formed crystals, which were fairly numerous. Most of the x-ray photographs were obtained with unfiltered copper radiation. Molybdenum radiation was used only for a few specimens with the object of determining intensities. Many of the crystals studied decomposed rapidly in air, particularly under the action of x-rays; it was necessary to photograph them after they had been coated with a layer of shellac varnish, which prolonged the life of the crystal appreciably.

The densities of most of the crystals were measured by hydrostatic weighing in Duboin's liquid; they lay in the range 1.70-2.90 g/cm³. For some of the specimens, the density was not determined experimentally, but was calculated on the assumption that the packing coefficient had the usual value of organic crystals, i.e., 0.7.

From the cell parameters found experimentally, we calculated the cell volume, the number of molecules that it contained, and the packing coefficient. The volume of a molecule, which was required for the calculation of the packing coefficient, was calculated on the assumption that the molecule consists of spherical segments described by the intermolecular radii. We made use of ideal models of the molecules and values of radii and bond lengths given in Communication 1 of this series of papers [1].

The results of the investigation are given in the table, which shows the cell parameters, the number of molecules per cell, the molecular weight, the x-ray and experimental values of the density (ρ_x and ρ_m), the position occupied by the molecule in the cell, the molecule's own symmetry in the crystal, the space group, the result of a piezoelectric test, the volume of the molecule, and the packing coefficient.

1,2,3,5-Tetrachlorobenzene (M.p. 54-55°) crystallizes well from ethanol and benzene in the form of thick transparent needles. The extinction angle referred to the lengthwise direction of the crystal (axis *a*) is 70.9°. The end faces are imperfectly formed; the main zone is formed by the faces of a rhombic prism $\{011\}$. In air, the crystals darken in color, and under the action of x-rays they are decomposed; the photographs were therefore taken with crystals covered with shellac. The number of molecules in a cell was found to be doubled, i.e., double the order of the space group.

1,2,3-Trichloro-5-nitrobenzene (M.p. 71°) crystallizes from ethanol in the form of fairly perfect thick pale-yellow plates having the shape of a parallelogram. The extinction angle referred to a long edge of the plate (axis *a*) is 35.8°. The simple forms are pinacoids $\{001\}$ (main faces of the plate), $\{010\}$, $\{01\bar{1}\}$, and $\{100\}$. The crystals are stable in air and to the action of x-rays. The angular constants of the triclinic cell were determined by means of x-rays, because the $\{100\}$ face is imperfect. The number of molecules in the cell is doubled. A sketch of the crystal is given in Fig. 1.

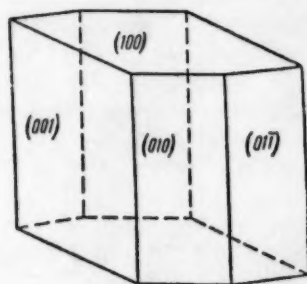


Fig. 1. Crystal of 1,2,2-trichloro-5-nitrobenzene.

3,4,5-Trichloroaniline Hydrochloride (M.p. 200-210° with decomp.) crystallizes poorly; from solutions in benzene and chloroform very fine yellow needles are precipitated. The most suitable solvent found was a 1 : 1 mixture of water and ethanol, from which thicker clear pale-yellow needles were grown. The extinction angle referred to the axis of the needle (axis *a*) is 8.0°. We did not succeed in measuring the end faces. The main zone is formed by the faces of a pinacoid $\{010\}$ and a rhombic prism $\{011\}$. The crystals are stable to the action of x-rays and photograph very well. From the intensities of reflections of the $Ok\bar{l}$ type, we calculated the Patterson projection and determined the coordinates of the chlorine atoms.

1,3-Dibromo-2-chlorobenzene (M.p. 73°) crystallizes readily from ethanol in the form of transparent rhombohedra. Under crossed nicols, the extinctions are along the diagonals of the rhombohedron; the angle between its edges is 112°. Simple forms: pinacoid $\{100\}$ and rhombic prism $\{111\}$. The number of molecules in a cell is doubled. It is isomorphous with 1,2,3-tribromobenzene and 1,3-dibromo-2-iodobenzene.

2-Bromo-1,3,5-trichlorobenzene (M.p. 64-65°) crystallizes from ethanol to thick transparent pale-yellow needles. Extinction is parallel to the lengthwise direction of the needle. The end faces give no reflections. The simple forms are tetragonal prisms $\{110\}$ (the most developed faces) and $\{100\}$. The crystals are stable to the action of x-rays and photograph very well with copper and molybdenum radiations. The molecules take up special positions on the symmetry planes.

1,2,3-Tribromobenzene (M.p. 87-88°) crystallizes in thick rhombic plates from ethanol (Fig. 2). The angle between the edges of the most developed rhombic face is 115°; extinction is along the diagonals of the rhombohedron. The simple forms are pinacoid $\{001\}$ and rhombic prism $\{111\}$. The crystals photograph well, but are decomposed under the prolonged action of x-rays. It is isomorphous with 1,3-dibromo-2-chlorobenzene and 1,3-dibromo-2-iodobenzene. The number of molecules in a cell is doubled.

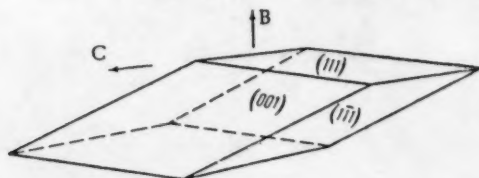


Fig. 2. Crystal of 1,2,3-tribromobenzene

1,3-Dibromo-2-iodobenzene (M.p. 99-100°) crystallizes in transparent rhombic plates from ethanol. The angle between the edges of the rhombohedron is 105°. The extinctions are along the diagonals of the rhombohedron. The simple forms are the pinacoid $\{001\}$ and rhombic prism $\{111\}$. The crystals photograph well, but are decomposed under the prolonged action of x-rays. It is isomorphous with 1,3-dibromo-2-chlorobenzene and 1,2,3-tribromobenzene.

Results of X-ray Investigation of Polyhalobenzenes and Derivatives

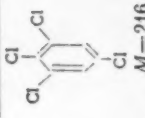
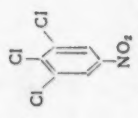
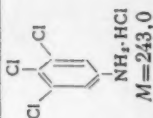
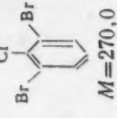
No.	Name	Structural formula and mol. wt.	Cell parameters (periods in Å)	Number of molecules in cell and their position	Symmetry of the molecule itself	Synony. space group, piezo effect	Volume of molecule (Å ³)	Packing coefficient k_p (n=no. of molecules)
1	1,2,3,5-Tetrachlorobenzene	 $M=216$	$a=3.84 \pm 0.01$ $b=23.99 \pm 0.10$ $c=17.08 \pm 0.03$ $\beta=92.5^\circ \pm 1^\circ$ $\rho_x=1.84$ $V=1572 \text{ Å}^3$	$n=8$ General, double value	mm	Monoclinic $P 2_1/c$; no piezo effect	143, 8	$k_3=0.73$
2	1,2,3-Trichloro-5-nitrobenzene	 $M=226.5$	$a=7.63 \pm 0.04$ $b=7.87 \pm 0.01$ $c=14.59 \pm 0.05$ $\alpha=67.42^\circ \pm 20'$ $\beta=81.14^\circ \pm 20'$ $\gamma=80.48^\circ \pm 20'$ $\rho_m=1.97$ $\rho_x=1.795$ $V=837 \text{ Å}^3$	$n=4$ General double value	mm or 2	Triclinic $P \bar{1}$; no piezo effect	145, 8	$k_4=0.70$
3	3,4,5-Trichloro-aniline hydrochloride	 $M=243.0$	$a=3.92 \pm 0.01$ $b=13.28 \pm 0.01$ $c=15.02 \pm 0.01$ $\beta=101.5^\circ \pm 0.5^\circ$ $\rho_x=2.45$ $V=757 \text{ Å}^3$	$n=4$ General	mm	Monoclinic $P 2_1/c$; no piezo effect	152, 1	$k_4=0.80$
4	1,3-Dibromo-2-chlorobenzene	 $M=270.0$	$a=12.84 \pm 0.05$ $b=8.38 \pm 0.06$ $c=15.49 \pm 0.10$ $\beta=113.30^\circ \pm 30'$ $\rho_x=2.37$ $V=1524 \text{ Å}^3$	$n=8$ General double value	mm	Rhombic $P 2_1/c$; no piezo effect	141, 5	$k_3=0.74$

TABLE (continued)

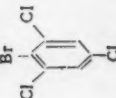
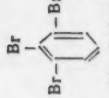
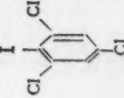
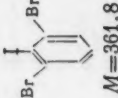
No.	Name	Structural formula and mol. wt.	Cell parameters (periods in Å)	Number of molecules in cell and their position	Symmetry of the molecule itself	Syngony, space group, piezo effect	Volume of molecule (Å ³)	Packing coefficient κ_n (n=number of molecules)
5	2-Bromo-1,3,5-trichlorobenzene	 M=280,4	$a=b=14,28 \pm 0,10$ $c=3,99 \pm 0,01$ $\rho_x=1,32$ $V=814 \text{ Å}^3$	$n=4$ Special position on the \bar{m} plane	mm	Tetragonal $P4_21m$; piezo effect occurs	150,2	$\kappa_{n4}=0,74$
6	1,2,3-Tri-bromobenzene	 M=314,8	$a=13,03 \pm 0,05$ $b=8,29 \pm 0,08$ $c=15,56 \pm 0,06$ $\beta=113^\circ \pm 1'$ $\rho_x=2,73$ $V=1546 \text{ Å}^3$	$n=8$ General, double value	mm	Monoclinic $P 2_1/c$; no piezo effect	147,9	$\kappa_{n8}=0,77$
7	1,3,5-Tri-chloro-2-iodobenzene	 M=307,4	$a=4,05 \pm 0,01$ $b=21,69 \pm 0,10$ $c=9,78 \pm 0,06$ $\beta=101^\circ 21' \pm 30'$ $\rho_m=2,3$ $\rho_x=2,44$ $V=842 \text{ Å}^3$	$n=4(3,77)$ General	mm	Monoclinic $P 2_1/c$; no piezo effect	156,4	$\kappa_{n4}=0,74$
8	1,3-Dibromo-2-iodobenzene	 M=361,8	$a=13,45 \pm 0,05$ $b=8,50 \pm 0,02$ $c=7,83 \pm 0,08$ $\beta=112^\circ \pm 1'$ $\rho_x=2,91$ $V=830 \text{ Å}^3$	$n=4$ General	mm	Monoclinic $P 2_1/a$; no piezo effect	154,1	$\kappa_{n8}=0,74$

TABLE (continued)

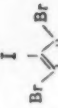
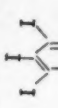
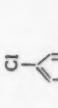
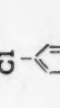
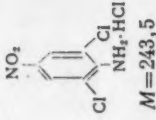
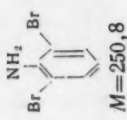
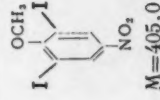
No.	Name	Structural formula and mol. wt.	Cell parameters (periods in Å)	Number of molecules in cell and their position	Symmetry of the molecule itself	Syngony, space group, piezo effect	Volume of molecule (Å ³)	Packing coefficient κ_n (κ =no. of molecules)
9	1,3-Dibromo-2-iodo-5-nitrobenzene	 $M=406,9$	$a=9,06 \pm 0,01$ $b=20,11 \pm 0,01$ $c=10,30 \pm 0,03$ $\beta=91^\circ \pm 1'$ $\rho_m=2,58$ $\rho_x=2,90$ $V=1876 \text{ Å}^3$	$n=8(7, 12)$ General, double value	mm or 2	Monoclinic $P 2_1/a$; no piezo effect	171,2	$\kappa_{n9}=0,73$
10	1,2,3-Triiodo-5-nitrobenzene	 $M=500,7$	$a=7,28 \pm 0,06$ $b=17,43 \pm 0,20$ $c=16,72 \pm 0,06$ $\beta=91^\circ 30' \pm 30'$ $\rho_m=2,84$ $\rho_x=3,15$ $V=2122 \text{ Å}^3$	$n=8(7, 21)$ General, double value	mm or 2	Monoclinic $P 2_1/c$; no piezo effect	183,5	$\kappa_{n10}=0,69$
11	1,3,5-Trichloro-2-nitrobenzene	 $M=226,5$	$a=8,87 \pm 0,06$ $b=12,32 \pm 0,05$ $c=7,87 \pm 0,04$ $\beta=109^\circ \pm 1'$ $\rho_m=1,77$ $\rho_x=1,77$ $V=857 \text{ Å}^3$	$n=4(4, 00)$ Special position on 2 axes	mm or 2	Monoclinic $A 2/a$; no piezo effect	145,8	$\kappa_{n11}=0,68$
12	2,4,6-Trichloroaniline	 $M=196,5$	$a=16,58 \pm 0,03$ $b=3,90 \pm 0,03$ $c=13,74 \pm 0,17$ $\beta=117^\circ \pm 1'$ $\rho_x=1,66$ $V=792 \text{ Å}^3$	$n=4$ General, double value	mm	Monoclinic $P 2_1$; no piezo effect	129,7	$\kappa_{n12}=0,66$

TABLE (continued)

No.	Name	Structural formula and mol. wt.	Cell parameters (periods in Å)	Number of molecules in cell and their position	Symmetry of the molecule itself	Syngony, space group, piezo effect	Volume of molecule (Å ³)	Packing coefficient k_n (n =no. of molecules)
13	2,6-Dichloro-4-nitroaniline hydrochloride	 M=243,5	$a=3,72 \pm 0,1$ $b=17,86 \pm 0,02$ $c=23,84 \pm 0,28$ $\beta=93^\circ \pm 1^\circ$ $\rho_x=2,06$ $V=1583 \text{ Å}^3$	$n=8$ General, double value	m or 2	Monoclinic $P2_1/c$ no piezo effect	154,1	$k_{n3}=0,78$
14	2,6-Dibromoaniline	 M=250,8	$a=16,43 \pm 0,05$ $b=4,43 \pm 0,01$ $c=10,31 \pm 0,02$ $\rho_x=2,23$ $V=750 \text{ Å}^3$	$n=4$ General	mm or m	Rhombic $P 2_1 2_1 2_1$; piezo effect occurs	127,4	$k_{n4}=0,68$
15	2,6-Diiodo-4-nitroanisole	 M=405,0	1) $a=15,25 \pm 0,04$ $b=16,35 \pm 0,08$ $c=8,43 \pm 0,03$ $\beta=98^\circ 50' \pm 30'$ $\rho_m=2,38$ $\rho_x=2,61$ $V=2077 \text{ Å}^3$ 2) $a=15,48 \pm 0,03$ $b=16,31 \pm 0,05$ $c=4,23 \pm 0,01$ $\rho_m=2,38$ $\rho_x=2,53$ $V=1068 \text{ Å}^3$	$n=8(7,31)$ General	m	Monoclinic $C 2/c$; no piezo effect	182,3	$k_{n5}=0,70$
		1) α -modification (plates); 2) β -modification (needles)		$n=4(3,77)$ Special on planes of symmetry	m	Rhombic $Pbam$ no piezo effect	182,3	$k_{n4}=0,69$

1,3,5-Trichloro-2-iodobenzene (M.p. 55°) crystallizes in colorless needles from petroleum ether and methanol. The extinction angle referred to the lengthwise direction of the needle is 22.3°. There are no end edges, and the main zone (axis *a*) is formed by the faces of a pinacoid {001} and rhombic prisms {011} and {021}. The crystals are quite stable to x-rays and give excellent photographs with copper and molybdenum radiations.

1,3-Dibromo-2-iodo-5-nitrobenzene (M.p. 135-136°) crystallizes from benzene in the form of brown elongated plates or prisms (Fig. 3); it is only slightly soluble in alcohol. The extinction angle referred to the lengthwise direction of the prism (axis *a*) is 75.7°. The simple forms are rhombic prism {011} and pinacoid {101}. The crystals are stable to x-rays. The number of molecules in the cell is doubled.

1,2,3-Trifluoro-5-nitrobenzene (M.p. 161-162°) crystallizes from ethanol and benzene in the form of yellow prisms, unstable in air. The end faces are ill-defined; the main zone (axis *a*) is formed by the faces of a rhombic prism {011}. The crystals are unstable under the action of x-rays, and it is difficult to obtain good photographs. The number of molecules in the cell is doubled.

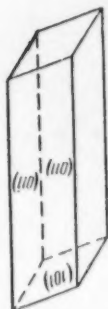


Fig. 3. Crystal of 1,3-Dibromo-2-iodo-5-nitrobenzene.

1,3,5-Trichloro-2-nitrobenzene (M.p. 70-71°) crystallizes well from ethanol and benzene in the form of thick needles and long plates. The extinction angle referred to the lengthwise direction of the crystal (axis *a*) is about 45°. Only the faces of the main zone, which belong to the simple forms of pinacoid {010} and rhombic prism {011}, are clearly defined. The crystals are stable in the air and to the action of x-rays. The Patterson projection on *bc* was calculated, and from this, the coordinates of the chlorine atoms were determined.

2,4,6-Trichloroaniline (M.p. 76-77°) crystallizes well from glacial acetic acid and aqueous alcohol in the form of colorless needles having direct extinction. Only faces of the main zone (axis *b*) are present, and these belong to the pinacoids {100}, {001}, and {101}. The crystals photograph well and are stable to x-rays. The extinctions indicate that space groups $P2_1$ and $P2_1/m$ are possible, but the second of these must be rejected because of the presence of a piezoelectric effect. Hence, the number of molecules in a cell (4) is double the order of the group.

2,6-Dichloro-4-nitroaniline Hydrochloride (M.p. 194-195°) crystallizes poorly (very fine yellow needles from methanol. The extinction angle referred to the lengthwise direction of the needle (axis *a*) is about 8°. Goniometric measurement could not be carried out because of the imperfect character of the crystals. The crystals decompose rapidly during the exposure. The number of molecules in a cell is doubled.

2,6-Dibromoaniline (M.p. 87-88°) crystallizes from ethanol in the form of transparent needles having direct extinction. Only faces of the main zone (axis *b*) could be measured on the goniometer; these belong to simple rhombic forms {101} and {201}. The crystals are unstable in the air, but photograph well when coated with shellac varnish.

2,6-Diiodo-4-nitroanisole (M.p. 134-135°). Two types of crystals are precipitated simultaneously from a saturated benzene solution in the range 18-25°: yellowish plates (Fig. 4) and colorless needles. X-ray investigation showed that they belong to two different modifications, α (plates) and β (needles), and that of $\alpha \rightleftharpoons \beta$ transition point must be found within this temperature range. The $\alpha : \beta$ ratio depends on the rate of crystallization. The imperfect face formation of the β -crystals does not permit goniometric measurement. For α -crystals, the extinction angle referred to the *a* axis (lengthwise direction) is 19°; the simple forms are the pinacoids {100}, {101}, and {010} and rhombic prisms {011} and {110}.

It is interesting to note that in 8 of the 16 crystals investigated, the number of molecules in a unit cell was found to be twice the order of the group, which indicates "association" between molecules in the crystal [2]. For all the compounds studied, the packing coefficient was fairly high. When one halogen was replaced by another, isomorphism occurred more rarely than might have been expected (only 1,3-dibromo-2-chlorobenzene, 1,2,3-tribromobenzene, and 1,3-dibromo-2-iodobenzene are isomorphous).

The authors express their sincere thanks to M. N. Demina for the synthesis of 13 compounds for investigation, to P. P. Shorygin for the presentation of 1,3-dibromo-2-iodo-5-nitrobenzene and 2,6-diiodo-4-nitroanisole crystals, and to A. A. Voronkov for the piezoelectric effect determinations on the crystals.

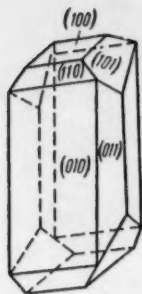


Fig. 4. Crystals of the α -form of 2,6-diiodo-4-nitroanisole.

SUMMARY

1. Goniometric measurements were carried out on polyhalobenzenes and their derivatives (15 compounds in all) having substantial steric hindrance in their molecules.
2. The unit cell parameters, the space groups, and some other crystallochemical characteristics of these crystals were determined.
3. 2,6-Diiodo-4-nitroanisole was shown to be dimorphous.
4. The coordinates of the heavy atoms were determined for two of the substances, (3,4,5-trichloroaniline hydrochloride and 1,3,5-trichloro-2-nitrobenzene), and the full structure was determined for one of the substances (2-bromo-1,3,5-trichlorobenzene).
5. From the substances studied, a selection was made of those showing the greatest promise for full structural analysis.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 27. ACTIVITIES OF UNPROMOTED COBALT CATALYSTS ON VARIOUS CARRIERS IN THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE, HYDROGEN, AND ETHYLENE

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The results reported in the preceding communication [1] show that an unpromoted Co-kieselguhr (kisatibi) catalyst is active in the synthesis of hydrocarbons from carbon monoxide, hydrogen, and ethylene, but has a high hydrogenating power. The object of the present work was to investigate the activity of an unpromoted cobalt catalyst on carriers other than kieselguhr in the same reaction.

EXPERIMENTAL

The apparatus and experimental procedure were as before [2]. The experiments were carried out in a flow system at 190° and atmospheric pressure with 1 : 1 mixtures of C₂H₄ and H₂ containing 4-6% CO. The space velocity of the original gas was about 100 hour⁻¹. The catalysts were usually prepared by precipitation with potassium carbonate from a cobalt nitrate solution in presence of carrier, and they were reduced with hydrogen at 450° for five hours. The catalysts contained 2.5-5.0 g of cobalt; the layer in the reaction tube was 20-40 cm in length. Compounds of various classes were used as carriers of the cobalt catalyst: metal oxides, hydroxides, carbonates, silicates and aluminosilicates, etc.

Calcium Hydroxide as Carrier. Catalyst 1, Co-Ca(OH)₂ (1 : 4), was quite inactive: neither liquid condensate nor gas oil was obtained. No gas contraction was observed (Table 1).

TABLE 1 Activity of Cobalt Catalyst on Various Carriers

Catalyst	Carrier	Time in work (hr.)	Space velocity (hr ⁻¹)	Contraction (%)	Total yield of hydrocarbons	
					(ml/cu.m)	(ml/liter-hr.)
1	Ca(OH) ₂	10	90	0,0	0,0	0,0
2	CaCO ₃	10	90	33,0	35,0	3,0
3	BaCO ₃	5	86	16,4	0,0	0,0
4	MgO	10	90	0,0	0,0	0,0
5	Cr ₂ O ₃	5	76	42,0	158,0	11,0
		5	76	33,0	36,0	2,5

Alkaline-earth Carbonates as Carriers. As Table 1 shows, Catalyst 2, Co-CaCO₃ (1:2), and Catalyst 3, Co-BaCO₃ (1:3), have some hydrogenating power (gas contraction 16.4-33.0%), but have no condensing power. The catalyst containing CaCO₃ is somewhat more active than the catalyst on a BaCO₃ carrier.

Magnesium Oxide as Carrier. Catalyst 4, Co-MgO (1:1), was found to be quite inactive in hydrogenation, and hypopolymerization (Table 1). The results cited show that calcium hydroxide, alkaline-earth carbonates, and magnesium oxide are unsuitable as carriers for a cobalt catalyst.

Chromic Oxide as Carrier. Catalyst 5, Co-Cr₂O₃ (1:4) had low activity and was completely unstable catalytically. After five hours in work, the activity fell sharply (Table 1).

Aluminum Oxide as Carrier. A previous communication [3] shows that aluminum oxide merits attention as a carrier for a Co-ThO₂ catalyst. Not only can the catalyst then obtained be regenerated, but on regeneration, it becomes more active than it is originally. Under these conditions, the yield of liquid condensate attains, on the average, 545 ml/m³ in the course of 22 hours (i.e., 43 ml/liter-hr.), and the yield of gas oil is 239 ml/m³.

It was of interest to investigate aluminum oxide as a carrier for an unpromoted cobalt catalyst in the same reaction. The results are given in Table 2. It should be noted that aluminum oxide itself shows neither condensing nor hydrogenating properties under the conditions of this reaction.

TABLE 2. Activities of Co-Al₂O₃ Catalysts

Catalyst	Composition of catalyst	Time in work (hr.)	Space velocity (hr ⁻¹)	Contraction	Total yield of hydrocarbons		Yield of gas oil
					(ml/cu.m)	(ml/l-hr.)	(ml/cu.m)
6	Co-Al ₂ O ₃ (1:2)	11	165	37	0	0	0
7	Co-Al ₂ O ₃ (5:1)	10	300	58	205	50.4	54
8	Co-Al ₂ O ₃ (1:5)	30	100	47	278	27.0*	135
8	Same, after regeneration	5	110	69	466	46.0	135
9	Co-Al ₂ O ₃ (1:5)	7	180	59	445	73.3	—
10	Ditto	15	80	52	291	20.7	75
10	Same, after regeneration	10	100	61	474	42.1	187
11	Co-Al ₂ O ₃ :C (1:1:1)	15	105	60	335	32.7	177

* Not counting gas oil.

Catalyst 6, Co-Al₂O₃ (1:2), was prepared by coprecipitation with potassium carbonate from a solution of cobalt and aluminum nitrates. This catalyst was completely without condensing properties, but it hydrogenated ethylene to ethane. From the data on the contraction and the compositions of the original and final gases, it was found that ethylene and hydrogen reacted to the extent of 60-65%; carbon monoxide did not react. Almost the whole of the ethylene that reacted was hydrogenated to ethane. No liquid condensate or gas oil was obtained.

Catalyst 7, Co-Al₂O₃ (5:1), was prepared by the same method as Catalyst 6. As will be seen from Table 2, increase in the relative amount of cobalt causes the catalyst to become quite active. At a space velocity of the original gas of 300 hr⁻¹, the yield of hydrocarbons may reach 50 ml/liter-hr. The hydrogenating power of the catalyst is lowered, and only about 50% of the ethylene that reacts is converted into ethane. Ethylene reacts to the extent of 86-89%, hydrogen to the extent of 72-89%, and carbon monoxide to the extent of 70-80%.

Catalyst 8, Co-Al₂O₃ (1:5), was prepared by precipitation from cobalt nitrate solution in presence of commercial Al₂O₃.

Catalyst 9 was the same as Catalyst 8, but one-half of the amount was taken.

Catalyst 10 was the same as Catalyst 8, but it was reduced at 450° for 3.5 hours, not five hours.

It will be seen from Table 2 that, in the range 400-450°, the reduction temperature has no particular effect on catalyst activity, if we neglect the somewhat greater yield of gas oil obtained over the catalyst reduced at 450°. As in the case of the promoted cobalt catalyst, after regeneration with hydrogen for five hours at 450°, a catalyst supported by aluminum oxide becomes more active than it was originally. Comparison of the activities of Co-ThO₂-Al₂O₃ (1 : 0.18 : 5) (see [3]) and Co-Al₂O₃ (1 : 5) shows that the addition of thorium to a Co-Al₂O₃ (1 : 5) catalyst increases its activity only slightly (average yields 26.5 and 27 ml/liter · hr., respectively, before regeneration and 43.4 and 42.1 ml/liter · hr., respectively, after regeneration).

Catalyst 11, Co-Al₂O₃-C (1 : 1 : 1), was prepared by the precipitation of cobalt nitrate solution with potassium carbonate in presence of a mixture of Al₂O₃ and activated charcoal. This catalyst was found to be active (Table 2).

Carriers Containing SiO₂. Catalyst 12, Co on silica gel, was prepared by treating silica gel with 5% cobalt formate solution at the boil for 20 minutes and then heating it (for decomposition of the formate and reduction) in a stream of hydrogen at 240°. As will be seen from Table 3, the catalyst was found to be inactive. The contraction was 10% at a space velocity of 94 hr⁻¹. Neither liquid catalyzate nor gas oil was obtained.

TABLE 3. Activities of Co Catalysts Deposited on Siliceous Carriers

Catalyst	Carrier	Time in work (hr.)	Space velocity (hr ⁻¹)	Contraction (%)	Total yield of hydrocarbons		Yield of gas oil (ml/cu.m)
					(ml/cu.m)	(ml/l · hr.)	
12	Silica gel	5	94	10	0	0	0
13	Silica gel (+Al ₂ O ₃)	5	100	0	0	0	0
14	Silica gel (+Al ₂ O ₃) (450°, air)	15	100	47	266	24,5	111
15	Co-silica gel (+Al ₂ O ₃)	25	50	60	347	17,1	100
16	Silica gel -Al ₂ O ₃	15	100	59	424	40,0	180
16	Same, after regeneration	5	100	67	465	42,8	193
17	Silica gel -MnO	20	100	56	364	34,1	127
18	Silica gel -Fe	5	60	11	0	0	0
19	Pumice	10	90	61	461	37,0	197
19	Pumice	5	82	56	191	14,2	115

Catalyst 13 (Co on silica gel and alumina). The carrier was finely ground silica gel impregnated with 2.5% aluminum nitrate solution and washed free from nitrate ions. Cobalt was deposited on this carrier in the usual way. The Co: carrier ratio was 1:1. The catalyst obtained was quite inactive; moreover, from its appearance, it could be concluded that it was not reduced by hydrogen.

Catalyst 14 differed from the preceding one only in that, before deposition of cobalt, the carrier was heated at 450° in a stream of air.

Catalyst 15 was prepared from Catalyst 13, after the latter had been in use; a new portion of cobalt was deposited on it in the usual way, and this was followed by treatment with hydrogen at 450°. This catalyst was found to be relatively active and stable.

Catalyst 16, Co-Al₂O₃-silica gel (1 : 1 : 1), was prepared by precipitation of cobalt from a solution of the nitrate with potassium carbonate in presence of a mixture of Al₂O₃ and silica gel. This catalyst was found to be the most active, but the increase in activity after regeneration was not very great. The respective average yields of liquid catalyzate before and after regeneration were 424 ml/m³ (40.0 ml/liter · hr.) and 465 ml/m³ (42.8 ml/liter · hr.), and the respective gas contractions were 59 and 67%.

Comparison of the properties of Catalysts 14 and 16 (Table 3) shows that the deposition of aluminum oxide on silica gel results in the formation of a much less effective carrier for a Co catalyst than the mixing of Al₂O₃ with silica gel followed by grinding in a mortar, as was done in the preparation of Catalyst 16.

Catalyst 17 (Co-silica gel-MnO) was prepared as follows. The carrier was precipitated with aqueous ammonia from 50% aqueous manganese nitrate solution in presence of silica gel. The product was washed free from nitrate ions, dried, and heated in a stream of air at 450° for three hours; the deposition of cobalt on the carrier was carried out in the usual way. The Co: carrier ratio was 1:2. This catalyst was found to be active.

Catalyst 18 differed from Catalyst 17 only in that iron nitrate was used instead of manganese nitrate in the preparation of the carrier. The catalyst was found to be inactive.

Catalyst 19, Co-pumice (1:2), was prepared from pumice that had been roasted at 700° in an electric furnace and ground to a powder. The catalyst was found to be fairly active, but of low stability; after ten hours in work, the activity of the catalyst fell sharply (Table 3).

Muslyumov Clay as Carrier. It has been shown previously [3] that Muslyumov clay, particularly when heated at 450°, is an effective carrier for a Co-ThO₂ catalyst: Its use results in an increase in the total yield of condensate and particularly of gas oil in the synthesis of hydrocarbons from carbon monoxide, hydrogen, and ethylene. It has been shown that a Co-Al₂O₃ (1:5) catalyst differs little in activity from a catalyst of the same composition, but promoted with thorium dioxide. There was therefore, reason to suppose that Muslyumov clay would be an effective carrier for an unpromoted Co catalyst. The results of experiments carried out with such catalysts are given in Table 4.

TABLE 4. Activities of Co-Muslyumov Clay Catalysts

Catalyst	Time in work (hr.)	Space velocity (hr ⁻¹)	Contraction (%)	Total yield of hydrocarbons		Yield of gas oil (ml/cu.m)
				(ml/cu.m)	(ml/liter-hr.)	
20	20	170	60	464	69	130
21	35	105	61	508	54	301
21*	65	110	63	498	51	281
21*	45	115	63	451	52	269
22	35	90	62	487	38	283
22*	60	90	66	483	38	280
22*	45	90	63	424	34	241

* Before this experiment the catalyst was regenerated with hydrogen at 450° for three hours.

Catalyst 20, Co-Muslyumov clay (1:2), was prepared by precipitation from cobalt nitrate solution in presence of Muslyumov clay that had been previously roasted at 450° for five hours; as usual, the catalyst was reduced with hydrogen at 450° for five hours. The experiments with this catalyst showed that it was active (yield of hydrocarbons 464 ml/m³).

Catalyst 21 differed from the preceding one only in that the clay was first heated at 450° for three hours in a stream of air.

Table 4 shows that with two three-hour regenerations of the catalyst with hydrogen at 450°, it worked at an almost constant level of activity for 145 hours, with an average total yield of condensate of 450-508 ml/m³ (51-54 ml/liter · hr.), at a space velocity of 105-115 liters/liter · hr. The gas contraction was 61-83%. The yield of gas oil was 270-300 ml/m³ on the average. Comparison of these results with those obtained with a catalyst of the same composition but promoted with ThO₂ [3] shows that in this case promoting has little effect on the activity of the catalyst. An unpromoted catalyst on Muslyumov clay regenerates well and is fairly stable. After 145 hours of work, the yield of condensate was still 51 ml/liter · hr., which is not much less than the average yield for 145 hours (53 ml/liter · hr.).

Catalyst 22 differed from Catalyst 21 in that the Co : Muslyumov clay ratio was 1 : 5. After being heated in a stream of air at 450° for four hours, the clay was treated in the cold with concentrated nitric acid for 15 hours and then washed free from Fe³⁺ and NO₃⁻ ions. Table 4 shows that the catalyst with the lower cobalt content was somewhat less active. In 140 hours of work, the average yield of condensate was 424-487 ml/m³ (34-38 ml/liter · hr.) at a space velocity of 90 hr⁻¹. The contraction was 62-66%. The average yield of gas oil was 241-283 ml/m³.

It will be seen from the results that Muslyumov clay heated in a stream of air at 450° is an extremely effective carrier for an unpromoted cobalt catalyst and endows the catalyst with high activity and catalytic stability.

An examination of our results shows that substances of basic character, such as calcium hydroxide, alkaline-earth carbonates, and magnesium oxide, are not effective as carriers for a deposited cobalt catalyst used in the synthesis of hydrocarbons from carbon monoxide, hydrogen, and ethylene. A catalyst deposited on chromic oxide was of low activity and was catalytically unstable. However, catalysts deposited on aluminum oxide has considerable activity. In this last case, the catalyst had to be prepared not by the coprecipitation of its components from a solution of cobalt and aluminum nitrates, but by the precipitation of the catalyst from cobalt nitrate solution in presence of aluminum oxide. The Co-Al₂O₃ catalyst is distinguished by the property of having a higher activity after regeneration than it had originally; its activity is close to that of the same catalyst promoted with thorium dioxide.

Silica gel was found to be an ineffective carrier. Silica gel impregnated with aluminum nitrate solution was also ineffective. However, when heated in a stream of air at 450°, it became a carrier of average activity (Catalyst 14). A 1 : 1 mixture of silica gel and aluminum oxide formed a very effective carrier, but the resulting catalysts could not be regenerated satisfactorily. A catalyst deposited on silica gel on which manganese hydroxide had been precipitated was found to be fairly active. Replacement of the manganese hydroxide by iron hydroxide resulted in a completely inactive catalyst. A catalyst in which pumice was used as carrier was active, but of low catalytic stability.

Muslyumov clay that had been heated at 450° in a stream of air was found to be the most effective of the carriers examined. Unpromoted Co catalysts deposited on this clay were distinguished by high activity and catalytic stability.

SUMMARY

1. Various substances were tried as carriers for an unpromoted cobalt catalyst used for the hydrocondensation of carbon monoxide with ethylene and the hypopolymerization of the latter under the action of carbon monoxide.

2. Ca(OH)₂, CaCO₃, BaCO₃, MgO, Cr₂O₃ and silica gel are ineffective. Al₂O₃ and silica gel containing deposited manganese oxide, a mixture of Al₂O₃ and silica gel, and particularly Muslyumov clay heated in a stream of air at 450° are extremely effective as carriers for this catalyst.

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* Original Russian pagination. See C. B. translation.

CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 5. COMPARATIVE STUDY OF THE ACTIVITIES OF NICKEL, COBALT, AND IRON CATALYSTS IN THE POLYMERIZATION OF PROPENE AND THE DEHYDROGENATION OF CYCLOHEXANE

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Aluminum oxide, silica gel, and synthetic aluminosilicates, and also nickel, cobalt, and iron and their oxides deposited on these substances, have frequently been tried as catalysts in the polymerization of simple olefins, in particular, ethylene [1] and the butenes [2]. The polymerization of propene over these catalysts has received relatively little study [3]. According to Lebedev and Filonenko [4], propene does not polymerize at room temperature and atmospheric pressure in presence of fuller's earth. According to Van Winkle [5], liquid propene gave an appreciable amount of liquid polymers when allowed to stand for two months under pressure in a sealed tube over activated fuller's earth. Gayer [6] showed that at 340-350° fuller's earth is an active catalyst the polymerization of propene, but a synthetic aluminosilicate obtained by impregnation of freshly prepared silica gel in aluminum sulfate solution and containing 1% of aluminum oxide was found to be many times as active. Nickel and NiO on kieselguhr [7], and on a synthetic aluminosilicate [8, 9], have been stated to be active catalysts for the polymerization of propene.

In the present investigation, we made a comparative study of the activities of nickel, cobalt, and iron catalysts on carriers in the polymerization of propene with the object of determining the parts played by compounds containing metals of Group VIII and by the carrier, as which we used aluminum oxide, glass, and a synthetic aluminosilicate (a cracking catalyst). After reduction with hydrogen, these catalysts were tested also for their activities in the dehydrogenation of cyclohexane with the object of resolving the question of whether the Group VIII metal oxide phase is preserved during the activation of the catalysts, or whether they combine completely with the carrier. In the case of nickel and cobalt catalysts, in the reduction with hydrogen, this phase should give the metal, which is active in the dehydrogenation of cyclohexane. After use, some of the catalysts were examined to determine their structural characteristics, the internal surface, the pore diameter, the total volume of the pores and the volume distribution with respect to diameters, and also the phase composition.

EXPERIMENTAL

The catalysts were prepared under conditions as similar as possible by the impregnation of aluminum oxide in the form of cylinders or powder, glass powder, and fine spherical grains of synthetic aluminosilicate with 10% solutions of nickel, cobalt, and ferric nitrates. The carriers were first dried to constant weight at 120° (six hours). Equal volumes of nitrate solution and carrier were used. After the impregnation, which was for seven hours at room temperature, the solution was decanted, and the mass remaining was dried at 120°, again to constant weight. The amount of adsorbed salt was determined by accurate weighing. When glass powder was used as carrier, the solution was not decanted, but the whole mass was evaporated on a water bath. Before the polymerization experiments, all the catalysts were activated in a stream of air at 450° for two hours, in the course of which the nitrates

were decomposed with formation of the corresponding Group VIII metal oxides. After each subsequent experiment, the catalysts were treated in the same way. Before experiments on the dehydrogenation of cyclohexane, the catalysts were activated or regenerated in a stream of hydrogen at 450° for two hours. The reactor consisted in a glass tube, diameter 10 mm, which was placed in a catalysis furnace fitted with a thermoregulator. Each experiment lasted two hours. The reaction products were trapped in two traps at 15° and at -40°, and the residual gas passed into a calibrated gas holder.

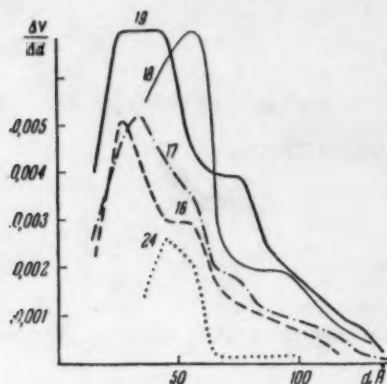


Fig. 1. Curves of the distribution of the volume of pores of the catalysts with respect to their diameters.

The original propene was prepared by the dehydration of isopropyl alcohol over aluminum oxide. The original cyclohexane had b.p. 80° (760 mm), n_D^{20} 1.4262; d_4^{20} 0.7782.

In the polymerization experiments, the space velocity of the original gas was varied in the range 200-500 hr⁻¹ for a catalyst volume of 1.5 ml. Cyclohexane was passed in a stream of hydrogen at a space velocity of 0.2 hr⁻¹ over 10 ml of catalyst at 300-350°. The benzene content of the catalyzate was determined from the values of n_D^{20} and d_4^{20} [10].

The structural characteristics of the catalysts were determined by the adsorption of benzene vapor at 20° in an apparatus containing a McBain-Bakr quartz balance [11]. The results are given in Table 1. The specific surfaces of the samples were calculated by the BET method [12], the pore diameter was calculated from Kelvin's formula without correction for the thickness of the adsorbed layer [13], and the total pore volume was calculated from the amount of benzene adsorbed at close to the saturation pressure. The curves for pore-volume distribution with respect to diameter are given in Fig. 1. The phase composition

was determined by x-rays (K_α of copper with Ni filter). In Table 1, the names not enclosed in parentheses are of phases that are undoubtedly present, and those in parentheses are of phases which may be present, but whose presence has not been unequivocally proved.

TABLE 1.

Catalyst	Specific surface (sq.m/g)	Pore Diameter (Å)	Volume of pores (cc/g)	Constant C in BET equation	Phase composition
8	2	Nonporous	0,01	—	NiO
24	380	45	0,29	17,0	γ -Al ₂ O ₃ , NiO (Ni, NiAl ₂ O ₄)
16	256	25	0,33	5,6	NiO, aluminosilicate
17	420	35	0,36	6,2	CoO, aluminosilicate
18	325	55	0,45	9,8	FeO, aluminosilicate
19	440	25-45	0,55	6,8	Aluminosilicate

Catalysts on Glass Powder as Carrier. Experiments on the polymerization of propene were carried out over nickel, cobalt, and iron catalysts on a glass-powder carrier at 276° and at a space velocity of 800-1200 hr⁻¹ with the object of determining the activities of Ni, Co, and Fe oxides. These catalysts, which contained, respectively, 3.1% Ni, 2.7% Co, and 1.7% Fe, were found to be quite inactive: No polymerization of propene was observed. Apart from propene, 1-2% of ethylene was found in the residual gas. Similar experiments were carried out over new portions of the same catalysts with an equimolecular mixture of propene and hydrogen at 200° at a total space velocity of 700-900 hr⁻¹. Again in these experiments, no polymerization of propene occurred. Moreover, scarcely any hydrogenation of propene occurred: The content of saturated hydrocarbons in the residual gas was over 0.7-1.2%. Of the catalysts reduced with hydrogen, only the nickel catalysts dehydrogenated cyclohexane (Table 1).

Hence, catalysts on glass powder as carrier are inactive both for the polymerization of propene (at 200-276°) and for the hydrogenation of propene (at 200°). It should be noted that these unreduced catalysts are of very low specific surface and have no porosity, as will be seen for the case of a nickel catalyst (Table 1, Catalyst 8).

Catalysts on Aluminum Oxide as Carrier. Experiments were carried out on the polymerization of propene over nickel, cobalt, and iron catalysts on aluminum oxide as carrier at 276° with a space velocity of 200-480 hr⁻¹. The contents of Group VIII metals of the catalysts were 2.5% Ni, 2.2% Co, and 1.8% Fe, respectively. Under these conditions, no polymerization of propene over cobalt and iron catalysts was observed, but over a nickel catalyst (Catalyst 24, Table 1) a liquid polymerizate was obtained in 0.4% yield on the original propene. On aluminum oxide itself as catalyst (5 ml of catalyst), no polymerization of propene occurred. Over new portions of catalyst of the same composition at 200-204° with a space velocity of 300-400 hr⁻¹, an equimolecular mixture of propene and hydrogen did not give a liquid polymerizate. In these experiments, there was also almost no hydrogenation of propene. The content of saturated hydrocarbons in the residual gas did not exceed 1.2%. In the dehydrogenation of cyclohexane, only the nickel catalyst was active (Table 2, Experiments 82-83).

TABLE 2. Experiments on the Dehydrogenation of Cyclohexane

Expt.	Catalyst			Reaction temp. (°C)	Space velocity of cyclohexane (hr ⁻¹)	Catalyzate		
	Composition	Ni content (%)	Catalyst No.			n_D^{20}	d_4^{20}	Benzene content
88	Ni-glass	1,2	43	300	0,22	1,4269	0,7792	1
89		1,2	43	300	0,10	1,4354	0,7895	16
82*	Ni-Al ₂ O ₃	4,2	39	300	0,21	1,4326	0,7855	11
83		4,2	39	330	0,24	1,4570	0,8194	51
80	Ni-aluminosilicate	2,2	35	300	0,24	1,4347	0,7878	15
81		2,2	35	350	0,23	1,4396	—	25
92**		2,5	47	300	0,17	1,4292	0,7817	5
93**		2,5	47	300	0,22	1,4370	0,7909	19
76***	Ni-aluminosilicate	2,3	38	300	0,31	1,4262	—	0,0
77***		2,3	38	350	0,19	1,4262	0,7782	0,0

* Before Expt. 82, the catalyst was reduced with hydrogen at 350° for 2.5 hours.

** Before Experiments 92 and 93, the catalyst was reduced with hydrogen at 450° for four hours.

*** Before Experiments 76 and 77, the catalyst was not reduced with hydrogen, but treated in a stream of air at 450°.

Catalysts on a Synthetic Aluminosilicate as Carrier. Experiments were carried out on the polymerization of propene over nickel, cobalt, and iron catalysts on a synthetic aluminosilicate having fine spherical grains, diameter about 0.2 mm, and also on the same aluminosilicate taken on its own at 276° with a space velocity of 200-1500 hr⁻¹. The results are given in Table 3 and Fig. 2.

Table 3 and Figure 2 show that an aluminosilicate has catalytic activity for the polymerization of propene, which is in accord with earlier investigations [5, 6]. The yield of liquid polymerizate in one passage was 12-15% by weight on the original propene. The yield of polymerizate fell somewhat with increase in the space velocity of propene. The activities of the iron and cobalt catalysts on aluminosilicate carrier were a little lower than that of the aluminosilicate itself taken as catalyst, and the yield of polymerizate fell with increase in space velocity. This fall was more marked for the cobalt catalyst than for the iron catalyst.

Hence, an additive containing iron or cobalt has a deactivating effect on an aluminosilicate. A nickel catalyst with an aluminosilicate carrier occupies a special position; at lower space velocities of propene, over this catalyst, the yield of polymerizate was more than twice as great as over the aluminosilicate itself, and it

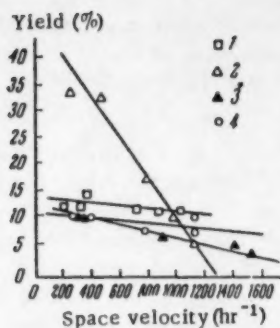


Fig. 2. Polymerization of propene over aluminosilicate catalysts without additions and with the addition of Ni, Co, or Fe: 1) Aluminosilicate; 2) Ni-aluminosilicate; 3) Co-aluminosilicate; 4) Fe-aluminosilicate.

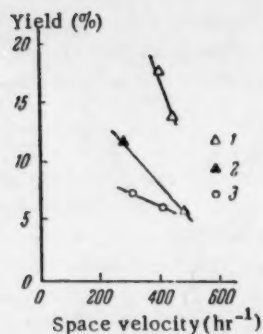


Fig. 3. Polymerization of a propene-hydrogen mixture over aluminosilicate catalysts with additions of Ni, Co, or Fe: 1) Ni-aluminosilicate; 2) Co-aluminosilicate; 3) Fe-aluminosilicate.

fell sharply with increase in space velocity. In these experiments the residual gas contained, apart from propene, 0.5-1.9% of ethylene and 1.3-3.0% of saturated hydrocarbons.

Fig. 1 shows that Catalysts 16 and 17 had pores similar to those of the aluminosilicate (Catalyst 19), though there were fewer of them. From Table 1 it will be seen that the effective pore diameter of Catalyst 18 was somewhat greater than that of Catalyst 19. On the x-ray diffraction diagrams of Catalysts 16, 17, and 18, there were in each case 1-2 uninterpreted lines, possibly the most intense lines of a product of reaction between the metal oxide and the aluminosilicate.

Experiments were carried out over new portions of these catalysts with an equimolecular mixture of propene and hydrogen at 276° with a total space velocity of 270-340 hr⁻¹ (catalyst volume 5 ml). The results are given in Table 4 and Fig. 3.

TABLE 3.

Expt.	Catalyst				Space velocity (hr ⁻¹)	Liquid polymerizate yield (% on original propene)
	Composition	Content of Group VIII metal (%)	Catalyst No.	Volume (ml)		
9	Ni-aluminosilicate	2,4	3	1,5	125	6,2
10		2,4	3	1,5	968	11,0
11		2,4	3	1,5	769	17,9
36		2,5	16	5,0	470	32,9
37		2,5	16	5,0	250	34,3
3	Co-aluminosilicate	2,4	1	1,5	1533	4,0
4		2,4	1	1,5	1400	5,3
5		2,4	1	1,5	900	6,9
39		2,3	17	5,0	330	11,6
40		2,3	17	5,0	330	11,6
6	Fe-Aluminosilicate	0,9	2	1,5	1033	11,0
7		0,9	2	1,5	1033	8,1
8		0,9	2	1,5	767	8,3
42		1,7	18	5,0	430	8,1
43		1,7	18	5,0	280	11,0
44		1,7	18	5,0	340	11,0
12	Aluminosilicate	—	4	1,5	1033	12,2
13		—	4	1,5	867	12,3
21		—	9	1,5	733	12,6
45		—	19	5,0	350	15,5
46		—	19	5,0	320	13,1
47		—	19	5,0	200	13,6

TABLE 4.

Expt.	Catalyst			Space velocity (hr ⁻¹)	Liquid polymerize yield (% on original propene)
	Composition	Content of Group VIII metal (%)	Catalyst No.		
55	Ni-aluminosilicate	2,4	25	390	17,9
56	Ditto	2,4	25	430	14,1
59	Co-aluminosilicate	2,4	27	270	11,8
60	Ditto	2,4	27	480	5,9
57	Fe-Aluminosilicate	1,3	26	300	7,6
58	Ditto	1,3	26	410	6,5

Table 4 and Fig. 3 show that a twofold reduction in the concentration of propene led to a twofold reduction in the yield of liquid polymerizate over a nickel catalyst with an aluminosilicate carrier. The yields of polymerizate over the cobalt and iron catalysts on the same carrier also fell with dilution of the propene, but not to such a great extent. Under these conditions, hydrogen did not react and was recovered almost completely in the residual gas, which contained about 40% of propene and 60% of hydrogen.

To determine the hydrogenating powers of nickel, cobalt, and iron catalysts on aluminosilicate carriers with partial or complete suppression of polymerization, we carried out experiments over them with an equimolecular mixture of propene and hydrogen at 200° with a total space velocity of 200-1500 hr⁻¹. Propene was hydrogenated to an extremely small extent. The hydrogen content of the residual gas was about 50%, and the content of saturated hydrocarbons was not more than 3-4%. Under these conditions, the activities of the catalysts were almost identical and extremely low for the polymerization reaction. The yield of liquid polymerizate was 1.5% at a space velocity of 1500 hr⁻¹ and about 6% at 200 hr⁻¹ (Table 5).

TABLE 5.

Expt.	Catalyst				Space velocity (hr ⁻¹)	Liquid polymerize yield (% on original propene)
	Composition	Content of Group VIII metal (%)	Catalyst No.	Volume (ml)		
26	Ni-aluminosilicate	2,6	11	1,5	833	1,5
27		2,6	11	1,5	1500	1,6
68		2,7	31	5,0	310	3,1
69		2,7	31	5,0	300	3,2
24	Co-aluminosilicate	2,6	10	1,5	933	1,3
25		2,6	10	1,5	1000	3,9
75		2,4	32	5,0	330	1,8
28	Fe-aluminosilicate	1,3	12	1,5	966	2,6
29		1,3	12	1,5	1233	2,0
72		1,4	33	5,0	200	5,9
73		1,4	33	5,0	400	3,0

In this case also, only the nickel catalyst was active for the dehydrogenation of cyclohexane (Table 1, Experiments 80, 81, 92, 93). However, a nickel catalyst that had not been reduced with hydrogen was not active in the dehydrogenation of cyclohexane.

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SUMMARY

1. Nickel, cobalt, and iron catalysts on glass, aluminum oxide, and synthetic aluminosilicate carriers were tried for the polymerization of propene at 276° and the hydrogenation of propene at 200°. The same catalysts, after reduction with hydrogen at 450°, were tried in the dehydrogenation of cyclohexane.

2. All the catalysts on glass-powder carriers were found to be inactive in all the reactions investigated, except that the nickel catalyst was active in the dehydrogenation of cyclohexane.

3. Of the catalysts on aluminum oxide carriers, only the nickel catalysts were active in the dehydrogenation of cyclohexane, and this had an extremely low activity in the polymerization of propene.

4. A synthetic aluminosilicate that was active in the polymerization of propene was partially deactivated when additions containing iron and cobalt were made. On addition of nickel, the yield of polymerizate increased at low space velocities of propene and fell greatly at high space velocities. Of all the aluminosilicate-based carriers tried, only the nickel catalyst was active in the dehydrogenation of cyclohexane.

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THERMAL TRANSFORMATIONS OF 2-METHYLFURAN IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

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Earlier, one of us, in collaboration with Nikitenkov [1], investigated the thermal transformation of alkylbenzenes in presence of hydrogen at high pressure but in absence of catalysts. Under the conditions studied there occurred not only cleavage of C-C bonds in a side chain, but also the removal of the whole alkyl group from the benzene nucleus (without hydrogenation of the latter). The radical-chain mechanism proposed [1] for the homogeneous destructive hydrogenation of aromatic hydrocarbons was later confirmed in a study of the thermal transformations of tetralin under a high pressure of hydrogen [2].

It was of interest to determine to what extent the behavior found in aromatic hydrocarbons would apply in the thermal transformations of alkylfurans (in particular, 2-methylfuran), at high pressures of hydrogen in absence of catalysts. Preliminary results on 2-methylthiophene [3] suggested a substantial difference in behavior under these conditions between aromatic hydrocarbons and heterocyclic compounds with "aromatic" properties. The present investigation confirmed this supposition. The results indicate also that there is a difference in composition between the products of the catalytic hydrogenation of 2-methylfuran [4], and those of its thermal transformations at high pressures of hydrogen in absence of catalyst.

EXPERIMENTAL

The experiments were carried out in a 120-ml reactor having a hydraulic seal by the procedure described previously [2] at 350-375° and working pressures of 240-750 atm. The initial hydrogen pressure was 100-400 atm. The duration of an experiment was two hours. In each experiment, the reactor was charged with 40 g of 2-methylfuran, freshly distilled over sodium through a column of 30-plate efficiency; b.p. 63.6-64.0°; n_D^{20} 1.4329. Two duplicate experiments were carried out under any given conditions. The reaction products were fractionated through the 30-plate column. Water was separated from the resulting fractions, which were dried with potassium carbonate; they were then refractionated to obtain narrower fractions, which were then examined for the presence of ketones and alcohols. To resolve some questions concerning the mechanism of the process under study, experiments were carried out also with 2-pentanone and 2-butanone under the conditions used with 2-methylfuran.

The experiments showed that already at 350°, 2-methylfuran underwent thermal transformations under a high pressure of hydrogen with formation mainly of high-boiling products, and also of a considerable amount of gaseous products. Apart from unchanged 2-methylfuran and water, only a relatively small part of the liquid products boiled below 170°. With rise in hydrogen pressure, the rate of the thermal transformations of 2-methylfuran increased. Rise in temperature up to 375° considerably increased the rate of the process. The results of the experiments are given in Table 1.

In the refractionation of the liquid products obtained at 375° at an initial hydrogen pressure of 400 atm, the following fractions were separated (Table 2).

TABLE 1. Thermal Transformation of 2-Methylfuran under a Pressure of Hydrogen

Temp. (°C)	Initial H ₂ pressure (atm)	Mean working pressure (atm)	Yield of liquid products						Water separa- ted	Gas + losses *
			Total	Including (b.p. in °C)						
				Up to 60	60-70	70-105	105-170	Resi- due		

(% by weight on 2-methylfuran taken)

350	400	240	92,8	1,5	71,9	0,7	2,2	12,6	0,6	10,6
350	300	550	89,3	3,1	55,6	2,6	5,0	20,1	1,1	12,5
350	400	750	84,0	3,0	45,0	2,5	5,4	24,8	1,9	17,4
375	400	720	70,6	6,4	16,5	6,1	4,3	33,1	3,5	30,1

* We estimate the total losses in the unloading of the reactor and the fractionation at 6-7%.

Fraction I consisted mainly of pentane. It was shown that acetone was present in Fraction III; it was identified as its 2,4-dinitrophenylhydrazone, m.p. 127-128°, undepressed by admixture of a known sample. Judging from the value of n_D^{20} , Fractions IV and V consisted mainly of 2-methylfuran. From Fraction VI, we obtained the 2,4-dinitrophenylhydrazone of 2-butanone, m.p. 114-115°, undepressed by admixture of a known sample. By re-fractionation of Fraction VIII, we isolated 2-pentanone, b.p. 101.5-102.0°, n_D^{20} 1.3928, and d_4^{20} 0.8090. The 2,4-dinitrophenylhydrazone, m.p. 141-142°, and the semicarbazone, m.p. 109-110°, were prepared; mixture tests showed no depression. Fraction IX contained 2-pentanol, identified by the preparation of its 3,5-dinitrobenzoic ester, m.p. 61.5°. Found: C 50.91; H 4.96; N 10.22%. $C_{12}H_{14}N_2O_6$. Calculated: C 51.04; H 5.00; N 9.93%.

TABLE 2. Results of Fractionation

Fraction	B.p. (°C)	n_D^{20}	% by wt.*	Fraction	B.p. (°C)	n_D^{20}	% by wt.*
I	28,6-40,0	1,3669	2,5	VIII	98,0-105,0	1,3949	17,0
II	40,0-55,0	1,3799	5,5	IX	105,0-120,0	1,4087	6,0
III	55,0-60,0	1,3990	10,3	X	120,0-125,0	1,4180	3,3
IV	60,0-65,0	1,4315	30,6	XI	125,0-134,0	1,4259	4,2
V	65,0-75,0	1,4258	6,3	XII	134,0-146,0	1,4320	2,6
VI	75,0-85,0	1,4136	2,6	XIII	146,0-162,0	1,4447	4,1
VII	85,0-98,0	1,4077	4,4				

* On total liquid products boiling up to 162°.

From Fraction XI, we obtained the 2,4-dinitrophenylhydrazone of 2-hexanone, m.p. 107-108°. Found: C 51.36; 51.61; H 5.66; 5.69; N 19.83; 20.03%. $C_{12}H_{16}O_4N_4$. Calculated: C 51.37; H 5.78; N 19.99%.

From this fraction, we also obtained the semicarbazone, m.p. 121-122°. Found: C 53.58; 53.57; H 9.51; 9.44; N 26.73; 26.81%. $C_7H_{15}ON_3$. Calculated: C 53.45; H 9.62; N 26.73%.

From Fraction XIII, we obtained the 2,4-dinitrophenylhydrazone of 2-heptanone, m.p. 89-90°. The literature [5] gives m.p. 89°. Found: C 52.74; H 5.73; N 19.51%. $C_{13}H_{18}O_4N_4$. Calculated: C 53.02; H 6.17; N 19.03%.

In the products of b.p. above 162°, we detected ketones of still higher molecular weight, which gave crystalline orange substances with 2,4-dinitrophenylhydrazine.

From the 200-210° fraction, we obtained a 2,4-dinitrophenylhydrazone of m.p. 239.5-240.5°, corresponding to acetophenone. Found: C 55.96; 55.83; H 4.36; 4.31; N 18.75; 18.56%. $C_{14}H_{12}O_4N_4$. Calculated: C 55.97; H 4.03; N 18.67%.

We did not succeed in isolating any other individual compounds from the high-boiling fractions. It may be supposed that the 190-200° fraction (mol. wt. 135; n_D^{20} 1.4876) contained phorone (b.p. 198.5°; mol. wt. 138.2; n_D^{20} 1.4998). Found: C 80.35; 80.41; H 9.62; 9.70%. $C_5H_{14}O$. Calculated: C 78.20; H 10.21%.

It follows from these results that in the thermal transformations of 2-methylfuran under a high pressure of hydrogen, an extremely complex mixture of products is formed, and much of this consists of ketones ranging from acetone to ketones with seven and more carbon atoms. We did not detect furan (b.p. 32°; n_D^{20} 1.4216), tetrahydrofuran (b.p. 65-66°; n_D^{20} 1.4020), or tetrahydro-2-methylfuran (b.p. 79-79.2°; n_D^{20} 1.4060) among the reaction products.

The gaseous products of the thermal transformations of 2-methylfuran consisted of carbon monoxide and methane hydrocarbons. The content of gaseous hydrocarbons was small relative to that of carbon monoxide, which was probably to be attributed to the participation of hydrocarbon radicals in alkylation reactions with formation of ketones of high molecular weight and other compounds. The thermochromatographic analysis of gaseous products obtained in reaction at 375° with an initial hydrogen pressure of 300 atm (duration of experiment two hours) gave the following results: H_2 82.37; CO 12.20; CH_4 4.25; C_2H_6 0.44; C_3H_8 0.12; C_4H_{10} 0.12; C_5H_{12} 0.07%.

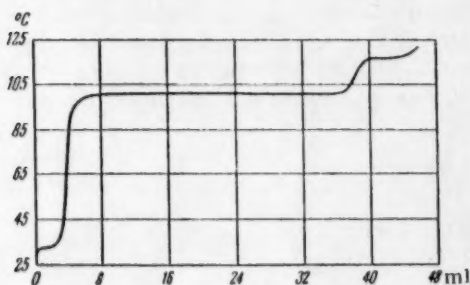


Fig. 1

We carried out experiments also with 2-pentanone at 375° for two hours with an initial hydrogen pressure of 300 atm. The original 2-pentanone had b.p. 101-102° and n_D^{20} 1.3910. After the experiments, 93% by weight (on 2-pentanone taken) of liquid products was unloaded from the reactor. The fractionation curve is shown in Fig. 1.

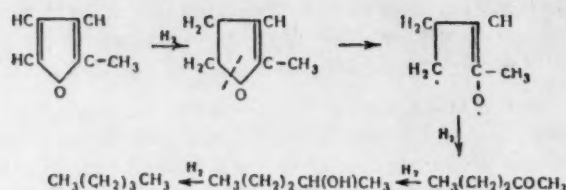
Examination of the fractionation curve shows, that the reaction product contains pentane, unchanged 2-pentanone, and 2-pentanol (fraction of b.p. 115-120°; n_D^{20} 1.4064). No acetone or butanone was detected. About 4% by weight of water was separated in the distillation.

An analogous result was obtained in the investigation of the transformations of 2-butanone at 375° for two hours with an initial hydrogen pressure of 400 atm. The original butanone had the following constants: b.p. 79.0-79.6°; n_D^{20} 1.3790; d_4^{20} 0.8050. From the reactor, we unloaded 92.4% by weight (on 2-butanone taken) of liquid products. By fractionation through a column, we isolated unchanged butanone, water, and more than 10% of sec-butyl alcohol, which was purified by refractionation; b.p. 98.5-99.5°; n_D^{20} 1.3972. Found: C 64.91; 64.97; H 13.76; 13.52%. $C_4H_{10}O$. Calculated: C 64.80; H 13.62%.

The 3,5-dinitrobenzoic ester had m.p. 75°, undepressed by admixture of a known sample. No acetone was detected in the reaction product. It should be noted that in the thermal decomposition of 2-pentanone and butanone under a high pressure of hydrogen, the formation of small amounts of products of b.p. above 120° was observed. Investigation of the gaseous products of the transformations of 2-pentanone, carried out by the thermochromatographic method gave the following results: H_2 93.41; CO 4.66; CH_4 0.45; C_2H_6 0.12; C_3H_8 0.24; C_4H_{10} 0.18; C_5H_{12} 0.15%.

EXPERIMENTAL RESULTS

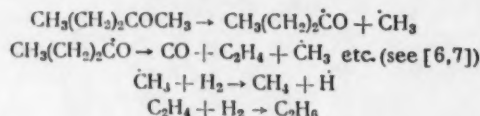
The main results obtained in the experimental part of this investigation may be stated as follows: 1) Unlike the homogeneous destructive hydrogenation of alkylbenzenes (see [1]), the thermal transformations of 2-methylfuran under high pressures of hydrogen proceed at lower temperatures and are not accompanied by appreciable elimination of the methyl group. 2) Unlike the hydrogenation of 2-methylfuran in presence of a nickel catalyst (see [4]), under our conditions, ketones are formed in which the number of carbon atoms may not only be equal to or less than, but also greater than the number in the original 2-methylfuran. 3) All the ketones identified had their carbonyl groups in the 2-position, which indicates that the cleavage of the C-O bond occurs at the 1,5-position in 2-methylfuran. 4) In the thermal transformations of 2-methylfuran under a pressure of hydrogen, large amounts of gaseous and high-boiling (b.p. above 170°) products are formed. Rise in the pressure of hydrogen accelerates the process. 5) Under the conditions studied, 2-pentanone is hydrogenated with formation of 2-pentanol and pentane; cleavage processes with formation of carbon monoxide and gaseous hydrocarbons, and also the formation of high-boiling products, occur to a much less extent than in the case of 2-methylfuran.



On the basis of the results, we may suggest the occurrence of the following stages in the thermal transformations of 2-methylfuran, under high pressures of hydrogen. It is probable that there first occurs the hydrogenation of 2-methylfuran to the 4,5-dihydro compound, which breaks down at the 1-5 bond. The biradical formed is hydrogenated with displacement of the double bond to 2-pentanone and further to 2-pentanol and pentane.

We consider it probable that 4,5-dihydro-2-methylfuran is formed under the conditions studied, though we did not isolate products of the partial or complete hydrogenation of 2-methylfuran. One of the grounds for this assumption is the acceleration of the transformations of 2-methylfuran with rise in the pressure of hydrogen. It may be noted also that, under similar conditions, tetrahydro-2-methylthiophene was detected among the products of the thermal transformations of 2-methylthiophene [3]. Moreover, in 4,5-dihydro-2-methylfuran, the 5-1 C-O bond must be considerably weaker than the 2-1 C-O bond, which is confirmed by the data on the composition of the reaction products. The above discussion, however, does not exclude the possibility of the cleavage of the 1-5 bond in 2-methylfuran itself.

The 2-pentanone formed can also undergo further thermal transformations:



Also, apart from gaseous hydrocarbons and carbon monoxide, high-boiling products are formed.

The results of the investigation showed a substantial difference in composition of products and rate of thermal transformation in the reactions of 2-methylfuran and 2-pentanone under high pressures of hydrogen. It may be supposed that this difference is associated with the high reactivity of the biradical $\text{H}_2\dot{\text{C}}-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\dot{\text{O}}$, which readily combines with alkyl radicals with formation, in particular, of higher ketones. It is possible that this biradical is also capable of cleavage reactions with formation of gaseous products, but this matter is in need of further investigation.

SUMMARY

1. An investigation was made of the thermal transformations of 2-methylfuran at 350-375° under high pressures of hydrogen. The liquid products were found to contain acetone, butanone, 2-pentanone, 2-hexanone, 2-heptanone, acetophenone, 2-pentanol, pentane, and water.
2. Under the given conditions, the thermal transformations of 2-methylfuran are accelerated by rise in the pressure of hydrogen and lead to the formation not only of the substances enumerated above, but also of considerable amounts of gaseous and high-boiling products (b.p. above 170°).
3. An investigation was made of the behavior of 2-pentanone under the conditions given above; it was hydrogenated with formation of 2-pentanol, pentane, and water.
4. The possible mechanism of the process studied was examined.

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BRIEF COMMUNICATIONS

HYDROPOLYMERIZATION OF ISOBUTENE OVER A COBALT-CLAY CATALYST UNDER THE JOINT ACTION OF HYDROGEN AND CARBON MONOXIDE

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Isobutene, unlike ethylene, propene, and 1- and 2-butenes, polymerizes to some extent (3-5%) over a Co-clay catalyst at 190° and atmospheric pressure [1]. The addition of hydrogen to the isobutene results in a considerable increase in the yield of liquid polymerization products: The yield is almost doubled by the addition of 0.2-0.3% of hydrogen and attains a maximum of 18% on the original olefin, when the hydrogen content of the original gas is 50%. Under these conditions, ethylene does not undergo any hydropolymerization at all, and propene and butene react only to the extent of 2% [2]. In presence of the carrier of the catalyst (clay), this effect of the addition of hydrogen to isobutene is not observed. Reaction of an equimolecular mixture of isobutene and hydrogen containing 5-6% of carbon monoxide over a Co-clay catalyst gave [3] a hydropolymerizate in about 40% yield on the olefin passed. However, there are as yet no data giving a direct indication of the effect of carbon monoxide on this process. The present investigation had the aim of studying the effect of carbon monoxide concentration and relative volumes of isobutene and hydrogen ($i\text{-C}_4\text{H}_8:\text{H}_2$) on the yield of isobutene hydropolymerizate.

EXPERIMENTAL

The apparatus, methods of preparing the starting materials, and experimental procedure were as described previously [1]. The Co-clay catalyst for the hydropolymerization of olefins under the action of carbon monoxide was used [4]. For comparison, red clay roasted at 450° in a stream of air was also tried as carrier for the catalyst [4]. The volume of catalyst in the glass reaction tube (diameter 10 mm) was 30 cc. All the experiments were of five hours' duration and were carried out at 190°, at atmospheric pressure and a space velocity of the original gas of 100 hr⁻¹ with freshly reduced or freshly regenerated catalyst.

Relation of the Yield of Isobutene Hydropolymerizate to the Carbon Monoxide Content of the Original Ternary Gas Mixture. A series of experiments was carried out with the same sample of catalyst and gas mixture for which $i\text{-C}_4\text{H}_8:\text{H}_2 = 3$ and which contained carbon monoxide at a concentration which was varied from 0.0 to 18% (Fig. 1a). An analogous series of experiments with another, much more active sample of catalyst was carried out on mixtures for which $i\text{-C}_4\text{H}_8:\text{H}_2 = 1$ and the CO content was varied from 0.0 to 20% (Curve 1b).

It will be seen from Fig. 1, that the relation of the yield of isobutene hydropolymerizate to the CO content of the original gas showed a sharp maximum at 2-4% CO, and the yield of liquid products attained 58%. Over the active sample of catalyst, an addition of 0.3-0.5% CO had already doubled the yield of hydropolymerizate (Fig. 1b). At a content of more than 8% of CO, hydropolymerization was retarded, and beyond this point it stopped altogether; and at 18-20% of CO, almost the whole of the liquid product, which was obtained in extremely small yields, was formed by the reaction of CO with H_2 , which was evident from the fact that the weight of this product was almost double the amount of polymerizate that could be formed from the isobutene that reacted. An analogous maximum at 6-8% of CO, with retardation of the hydropolymerization reaction at higher CO concentrations, was observed previously [2] for propene and butene.

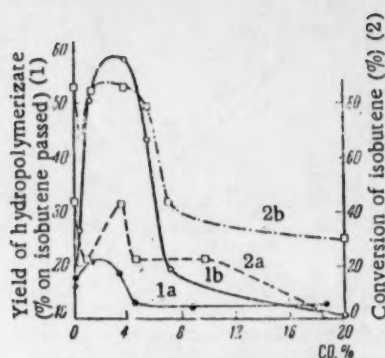


Fig. 1. Effect of the CO content of the original gas on the yield of liquid polymerizate (on the amount of isobutene passed) (1) and on the proportion of the isobutene that reacts (2) for $i\text{-C}_4\text{H}_8:\text{H}_2=3$ (a) and $i\text{-C}_4\text{H}_8:\text{H}_2=1$ (b).

isobutene over clay has an ionic character, whereas, over a Co-clay catalyst, the process appears to proceed by a free-radical mechanism. In this case, the initiators of the hydropolymerization of isobutene are probably its half-hydrogenated forms (isobutyl radicals) formed on the surface of the catalyst. On addition of small amounts of CO, it is hydrogenated with the formation of more active, probably methylene, radicals, which lead to more vigorous hydropolymerization of isobutene. Large amounts of CO lead to the adsorptional displacement of other components and a weakening of the reaction.

Polymerization in Presence of Clay

Content in original gas (percent by volume) of			Amount of isobutene that reacted (%)	Yield of liquid polymerizate (percent by weight) on	
isobutene	hydrogen	carbon monoxide		isobutene passed	isobutene that reacted
99,8	0,0	0,0	26,3	25,2	95,8
73,8	25,4	0,0	27,7	21,5	77,6
73,8	21,4	3,8	28,4	21,6	76,1

Effect of the Relative Amounts of Isobutene and Hydrogen in the Original Ternary Mixture on the Yield of Isobutene Hydropolymerizate. A series of experiments was carried out over a fresh portion of the first sample of catalyst with gas mixtures in which the content of CO was 4% and the $i\text{-C}_4\text{H}_8:\text{H}_2$ ratio was varied from 0.5 to 10 (Fig. 3). The maximum yield of liquid reaction products on the amount of isobutene passed was obtained when $i\text{-C}_4\text{H}_8:\text{H}_2=2$. When the ratio was lowered, the yield fell and the proportion of isobutene that reacted rose because of increased hydrogenation. A similar maximum was previously [5] observed for ethylene at a $\text{C}_2\text{H}_4:\text{H}_2$ ratio of 2.5-3.

SUMMARY

1. A study was made of the relation of the yield of products of the hydropolymerization of isobutene over a Co-clay catalyst at atmospheric pressure and 190° to the carbon monoxide concentration and the relative amounts of isobutene and hydrogen in the original gas mixture.

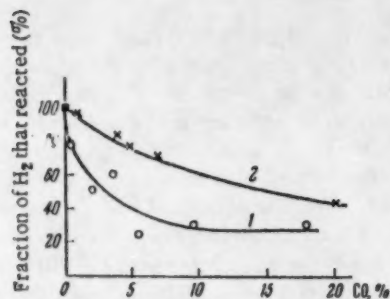


Fig. 2. Relation of the fraction of hydrogen that reacted (%) to CO content of original gas: 1) Over first sample of catalyst; 2) over second sample of catalyst.

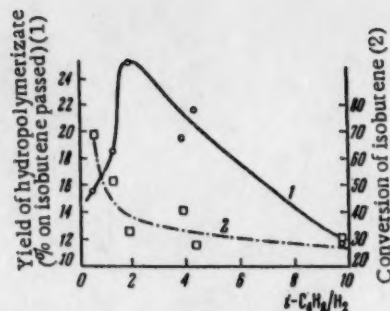


Fig. 3. Effect of the $i\text{-C}_4\text{H}_8:\text{H}_2$ ratio in the original gas on the yield of liquid hydropolymerizate (on the amount of isobutene passed) (1) and on the proportion of the isobutene that reacted (2). The CO content of the original gas was 4%.

2. The maximum yield of hydropolymerizate was obtained with 2-4% of CO in the original mixture and an $i\text{-C}_4\text{H}_8:\text{H}_2$ ratio of 2.

3. Over a clay catalyst, neither hydrogen nor carbon monoxide has any effect on the course of the polymerization of isobutene.

4. On the basis of the results, it is suggested that the hydropolymerization of isobutene over Co-clay has a free-radical mechanism and that polymerization over a clay catalyst has an ionic mechanism.

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*Original Russian pagination. See C. B. translation.

SOME PROPERTIES OF p-(TRIMETHYLSILYL)BENZALDEHYDE

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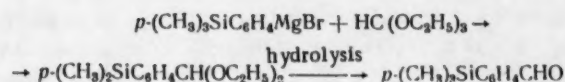
Original article submitted July 2, 1959

Some silicon-containing aldehydes [1] have been reported in the literature, in particular o-, m-, and p-(trimethylsilyl)benzaldehydes [2, 3] and p-(triphenylsilyl)benzaldehyde [4]. However, the properties of (trialkylsilyl)benzaldehydes have received scarcely any study. It has been reported that p-(trimethylsilyl)benzaldehyde reacts with 2,4-dinitro- and p-nitro-phenylhydrazines, steam-distills from acid solution without cleavage of the Si-C_{ar} bond, passes into the acid when exposed to air, and undergoes autoxidation [2, 3]. Still less is known about p-(triphenylsilyl)benzaldehyde: Its oxime and thiosemicarbazone have been prepared [1].

None of these investigations had the object of studying the properties of (trialkylsilyl)benzaldehydes. The present investigation was devoted to the study of some properties of p-(trimethylsilyl)benzaldehyde.

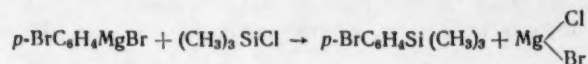
EXPERIMENTAL

p-(Trimethylsilyl)benzaldehyde was prepared by organomagnesium synthesis as follows [1]:



The synthesis was carried out in an atmosphere of nitrogen. The yield of pure p-(trimethylsilyl)benzaldehyde, b.p. 118-119° (15 mm), was 60-65%; n_D^{20} 1.5245; d_4^{20} 0.9865; found MR 55.35; calculated MR 54.73. Found: Si 15.81; 15.77%; C₁₀H₁₄SiO. Calculated: Si 15.75%. The literature gives: b.p. 119° (15 mm) [1]; b.p. 118° (15 mm), n_D^{20} 1.5245, and d_4^{20} 0.9862 [2].

The starting material, (p-bromophenyl)trimethylsilane, was prepared as follows [5]:



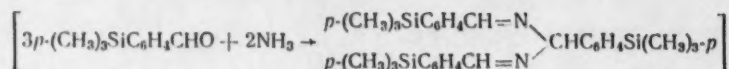
The yield of pure (p-bromophenyl)trimethylsilane, b.p. 116.8-117.2° (7 mm), was 35-40%; n_D^{20} 1.5302; d_4^{20} 1.2202; found MR 58.01; calculated MR 58.70. Found: Si 12.15; 12.35%; C₉H₁₃Br. Calculated: Si 12.25%. The literature [5] gives: b.p. 146-148° (50 mm); d_4^{20} 1.2197; n_D^{20} 1.5302.

p-(Trimethylsilyl)benzaldehyde is a colorless liquid of characteristic odor which gives qualitative reactions typical of the carbonyl group. Thus, we obtained the silver-mirror reaction and a color reaction with Schiff's reagent. With sodium bisulfite, p-(trimethylsilyl)benzaldehyde readily gave a bisulfite compound, a white crystalline powder, m.p. 154-155°. On treatment with dilute acids (8-10%), the bisulfite compound was decomposed quantitatively with formation of pure p-(trimethylsilyl)benzaldehyde, b.p. 188° (15 mm) and n_D^{20} 1.5245.

Also, with an alcoholic solution of hydroxylamine prepared from hydroxylamine hydrochloride it gave the oxime, a white crystalline powder, m.p. 62-63°; with 2,4-dinitrophenylhydrazine, it gave the 2,4-dinitrophenylhydrazone, which formed orange crystals, m.p. 220° (the literature [1] gives m.p. 209°); and with semicarbazide it gave the semicarbazone, a white crystalline powder, m.p. 199.5°.*

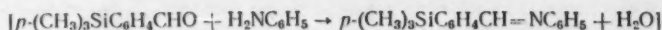
p-(Trimethylsilyl)benzaldehyde readily undergoes addition reactions with ammonia and aromatic amines.

Synthesis of 4,4',4''-Tris(trimethylsilyl)hydrobenzamide



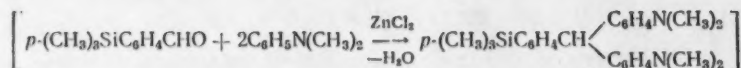
Ammonia, dried over caustic alkali, was passed for five hours into 5.4 g (0.03 mole) of p-(trimethylsilyl)benzaldehyde. The aldehyde-ammonia so obtained (in a yield of 14.1 g, i.e., 91.3%) was crystallized twice from alcohol and then formed a white crystalline powder, m.p. 110-111°. Found: Si 16.39; 16.55; C 69.96; 69.78; H 8.49; 8.41%. mol. wt. 510.82. $\text{C}_{30}\text{H}_{42}\text{Si}_3\text{N}_2$. Calculated: Si 16.36; C 69.97; H 8.22%; mol. wt. 514.95.

Synthesis of N-p-(Trimethylsilyl)benzylideneaniline



A mixture of 3.6 g (0.02 mole) of p-(trimethylsilyl)benzaldehyde and 1.9 g (0.02 mole) of freshly distilled aniline [b.p. 183.7° (757.2 mm)] was heated in a water bath for four hours. Vacuum distillation gave 4.9 g (96%) of N-p-(trimethylsilyl)benzylideneaniline, a slightly yellowish viscous liquid; b.p. 193.5-194.0° (6 mm); n_D^{20} 1.6130; d_4^{20} 1.0492. Found: Si 11.07; 10.70; C 73.83; 73.72; H 7.51; 7.21%. $\text{C}_{16}\text{H}_{19}\text{SiN}$. Calculated: Si 11.08; C 75.83; H 7.56%.

Reaction of p-(Trimethylsilyl)benzaldehyde with N,N-Dimethylaniline



p-(Trimethylsilyl)benzaldehyde (9 g, 0.05 mole) and freshly distilled N,N-dimethylaniline [12 g, b.p. 192-193.5° (758.1 mm)] were mixed in a porcelain dish with 5 g (0.037 mole) of anhydrous zinc chloride. The mixture was heated with stirring for four hours in a water bath. The resulting dark green viscous mass was purified from unchanged starting materials by steam distillation. The residue from the steam distillation was crystallized from ethanol. We obtained a silicon-containing leuco compound of the leuco-Malachite Green type, a white powder, m.p. 162.5-164.4°. Found: Si 7.18; 6.67; C 82.87; 82.90; H 8.00; 8.15%. $\text{C}_{26}\text{H}_{34}\text{SiN}_2$. Calculated: Si 6.96; C 83.60; H 7.92%.

The leuco compound was oxidized in a known manner.

From 5 g of the leuco compound, we obtained 4 g of the double salt of the dye with zinc chloride. The product was a silicon-containing dye of the type and color of Malachite Green. The zinc chloride compound of the dye has m.p. 220° and is readily soluble in water, alcohol, and ether. The properties of the dye are being studied.

We have also obtained a silicon-containing leuco compound of the leuco-Benzoaurine type. The results of the investigation will be published later.

SUMMARY

1. Some properties of p-(trimethylsilyl)benzaldehyde were studied. It gives characteristic qualitative reactions of carbonyl compounds (silver mirror and reaction with Schiff's reagent) and freely gives addition and condensation reactions with sodium bisulfite, 2,4-dinitrophenylhydrazine, semicarbazide, hydroxylamine, ammonia, and aromatic amines.

* The oxime, 2,4-dinitrophenylhydrazone, and semicarbazone were prepared by a procedure described in the literature [6].

2. The bisulfite compound, carbazone, and oxime of p-(trimethylsilyl)benzaldehyde were prepared for the first time, as also were 4,4',4''-tristrimethylsilylhydrobenzamide and N-p-(trimethylsilyl)benzylideneaniline.

3. It was shown that it is possible to prepare silicon-containing dyes of the triphenylmethane series.

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EFFECT OF MOLECULAR STRUCTURE ON DEHYDROGENATION IN THE CASE OF C_2 AND C_5-C_9 ALCOHOLS

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In previous papers [1], we reported results on the kinetics of the dehydrogenation of alcohols of various structures and established certain relations between the kinetic and adsorption characteristics and the structures of the molecules of the alcohols that were dehydrogenated. In the present investigation, we studied the dehydrogenation kinetics of the case of ethyl alcohol and normal primary alcohol from pentyl to nonyl.

EXPERIMENTAL

The experimental procedure was the same as in the previous work. The experiments were carried out over the same oxide catalyst, which has been shown to bring about the dehydrogenation of alcohols in a selective fashion without appreciable formation of dehydration or decomposition products. The reaction rate was determined from the volume of hydrogen liberated. There was a close correspondence between the amounts of hydrogen liberated and the amounts of aldehyde formed. Absolute ethyl alcohol was used, and the C_5-C_9 alcohols were dried with magnesium methoxide [2], distilled through a column of 60-plate efficiency, and distilled also under reduced pressure. Aldehydes for experiments with binary alcohol-aldehyde mixtures, which had the object of determining relative adsorption coefficients, were isolated from the catalyzates, dried, and distilled. The constants of the alcohols investigated are given in Table 1. Experiments with alcohols were carried out in the temperature range 300-360° at rates of passage of 1 and 1.4 ml of alcohol in 5 minutes.

Ethyl Alcohol. The extent of the conversion of alcohol into aldehyde in the range 318-398° was 10.9 to 62.7% (Table 2). Experiments with binary alcohol-aldehyde mixtures were carried out at 325-360° with $\bar{v}=1$ ml in 5 minutes. It was found that the relative adsorption coefficient of acetaldehyde varies with temperature from 6.2 at 325° to 2.6 at 360° (Table 3).

Pentyl Alcohol. The experiments were carried out at 302-380° with $\bar{v}=1$ and 1.4 ml in 5 minutes (Table 2). The conversion of alcohol into aldehyde was 10.7-55%. The relative adsorption coefficient of the aldehyde in the range 303-360° at $\bar{v}=1.4$ ml in 5 minutes varied from 11.6 to 2.4 (Table 3).

Hexyl Alcohol. The rate of dehydrogenation of the alcohol was measured at 308-386°. The conversion of the alcohol was 15.5-64% (Table 2). Binary alcohol-aldehyde mixtures were passed over the catalyst at 309-360° with $\bar{v}=1$ ml in 5 minutes; adsorption coefficients of the aldehyde varied from 7.5 to 2.7 (Table 3).

Heptyl Alcohol. The conversion of alcohol in the range 302-360° at $\bar{v}=1.4$ ml in 5 minutes was 14.2 to 49.7% (Table 2). The relative adsorption coefficient of the aldehyde, measured under the same conditions, varied from 11.0 to 2.7 (Table 3).

TABLE 1. Physical Constants of Alcohols and Aldehydes

Substance	Starting substance			Data in literature [3, 4]		
	B.p. (°C)	d_4^{20}	n_D^{20}	B.p. (°C)	d_4^{20}	n_D^{20}
Alcohols						
Ethyl	78,0	0,7903	1,3614	78,3	0,7900	1,3614
Pentyl	136,8—137,3	0,8146	1,4100	137—137,8	0,8147	1,4099
Hexyl	155,1—155,8	0,8196	1,4188	155—156	0,8204	n_D^{25} 1,4191
Heptyl	176,0—176,5	0,8180	1,4230	176,3—176	d_4^{22} 0,8173	n_D^{22} 1,4232
Octyl	194,5	0,8268	1,4296	195,2	0,8270	n_D^{24} 1,4343
Nonyl	213,5	0,8284	1,4343	213,5	d_4^{25} 0,8280	n_D^{15} 1,4358
Aldehydes						
Acetaldehyde	20,3		1,3315	20,8	0,780	1,3316
Valeraldehyde	103,8—104	0,8133	1,3985	103,4	$d_4^{11,2}$ 0,8185	n_D^{15} 1,4003
Hexanal	131—132,5	0,8152	1,4160	131	0,8176	1,4039[5]
Heptanal	152,5—153,5	0,8138	1,4175	152,8—153,2	0,8174	n_D^{19} 1,4137
Octanal	164—165	0,8267	1,4214	167—170	0,8258	1,4217
Nonanal	94 (22 mm)	0,8365	1,4365	93,5 (23 mm)	$d_4^{17,5}$ 0,8390	$n_D^{17,5}$ 1,4276

TABLE 2. Dehydrogenation of Normal Primary Alcohols

Alcohol	Temp. (°C)	Vol. of H ₂ (STP) liber- ated in 5 min. (ml)	Degree of dehydrogen- ation from vol. of H ₂ (%)	Analysis of gas (% by vol.)			
				CO ₂	C ₂ H ₄	H ₂	
1	2	3	4	5	6	7	
Ethyl	Feed of 1 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1 ml 385 ml						
	325	56,1	14,5	1,2	1,0	Not determined	
	338	73,7	19,1	1,2	1,6		
	360	112,0	29,1	1,8	2,2		
	375	157,7	40,9	2,4	2,4		
	398	241,5	62,7	2,8	3,0		
	Feed of 1.4 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1.4 ml 539 ml						
	318	58,8	10,9	1,0	0,8	98,2	
	339	102,7	19,1	1,2	1,2	97,6	
	361	164,7	30,5	1,6	2,2	96,2	
	384	259,9	48,2	2,4	2,8	94,8	
	Pentyl	Feed of 1 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1 ml 207 ml					
		302	22,4	10,8	0,2	Nil	99,8
320,5		35,2	17,0	0,4	»	99,6	
342		64,9	31,3	0,4	»	99,6	
361		94,9	45,6	0,6	»	99,4	
Feed of 1.4 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1.4 ml 290 ml							
303		32,0	11,0	0,4	Nil	99,6	
320		53,0	21,8	0,6	»	99,4	
345		85,0	29,4	0,6	»	99,4	
360		116,0	40,0	0,6	»	99,4	
380		160,0	55,0		Not determined		

TABLE 2. (continued)

Alcohol	Temp. (°C)	Vol. of H ₂ (STP) liberated in 5 min. (ml)	Degree of dehydrogenation from vol. of H ₂ (%)	Analysis of gas (% by vol.)		
				CO ₂	C ₂ H ₄	H ₂
1	2	3	4	5	6	7
Hexyl	Feed of 1 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1 ml 180 ml					
	309	28,0	15,5	0,8	Nil	99,2
	340	53,0	29,4	1,0	»	99,0
	345	58,0	32,2	1,0	»	99,0
	360	76,0	42,2	1,0	»	99,0
	386	116,0	64,4	2,2	»	97,8
	Feed of 1.4 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1.4 ml 252 ml					
	319	46,0	18,2	0,8	Nil	99,0
	340	68,0	27,0	1,2	»	98,8
	361	101,0	40,1	1,0	»	99,0
	381	138,0	54,7	2,2	»	97,8
Heptyl	Feed of 1.4 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1.4 ml 221.2 ml					
	302	31,5	14,25	Nil	Nil	100
	320	52,0	23,5	0,2	»	100
	340	77,0	34,8	0,4	»	99,6
	360	110,0	49,7	0,6	»	99,6
Octyl	Feed of 1 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1 ml 141.2 ml					
	280	40,3	7,3	Nil	Nil	Not determined
	322	32,3	22,8	0,4	»	99,6
	342	52,3	37,3	0,4	»	99,6
	360	70,2	49,8	0,6	»	99,3
	Feed of 1.4 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1.4 ml 197 ml					
	283	45,5	7,8	Nil	Nil	Not determined
	300	26,0	13,1	0,2	»	99,8
	318	40,7	20,5	0,4	»	99,4
	340	63,0	32,0	0,4	»	99,6
	360	88,0	44,6	0,4	»	99,6
Nonyl	Feed of 1 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1 ml 128.8 ml					
	280	9,8	7,7	Nil	Nil	100
	320	30,5	23,6	»	»	100
	342	50,0	38,8	0,4	»	99,6
	360	66,0	51,2	0,4	»	99,6
	Feed of 1.4 ml of alcohol in 5 min.; theoretical vol. of H ₂ from 1.4 ml 180.3 ml					
	303	22,0	12,2	Nil	Nil	100
	320	36,0	20,0	0,4	»	99,6
	340	55,0	30,4	0,6	»	99,4
	360	80,0	44,4	0,6	»	99,4

Octyl Alcohol. The experiments were carried out in the range 280-380° at $\gamma = 1$ and 1.4 ml in 5 minutes. The degree of dehydrogenation of the alcohol was 7.3-67% (Table 2). The relative adsorption coefficient of the aldehyde, measured at 300-360° with $\gamma = 1.4$ ml of mixture in 5 minutes, varied from 7.7 at 300° to 2.6 at 360° (Table 3).

TABLE 3. Adsorption Coefficients of Aldehydes, and Thermodynamic Functions Calculated from Them

Aldehyde	Temp. (°C)	Alcohol content of mix- ture (%)	m_s	m	z_1	ΔF (cal)	ΔH (kcal)	ΔS (cal/degree mole)
1	2	3	4	5	6	7	8	9
Acetaldehyde	330	79,0	62	26	5,3	-1995	13,5	25,7
	345	79,0	85	45	3,4	-1500		24,3
	360	79,0	112,2	66,7	2,6	-1200		23,2
	325	79,0	56,1	21,5	6,2	-2125		26,1
Valeraldehyde	303	80,0	32	8,4	11,6	-1627 -1537 -1100	14,2	26,7
	320	80,0	53	21,8	5,7			25,5
	345	80,0	85	45,3	3,5			24,2
	360	80,0	116	72,5	2,4			
Hexanal	309	80,0	28	9,6	7,5	-1920 -1527 -1248	13,5	25,6
	328	80,0	41,5	18,5	5,0			24,4
	345	80,0	58	31	3,5			23,4
	360	80,0	76	45,5	2,7			
Heptanal	302	80,0	31,5	8,6	11,0	-2027 -1624 -1248	13,5	26,2
	320	80,0	52	21,7	5,6			24,5
	340	80,0	77	39,5	3,8			23,4
	360	80,0	110	65,3	2,7			
Octanal	300	77,5	26	8,0	7,7	-2027 -1624 -1500 -1200	14,2	27,4
	320	77,5	43	16,3	5,6			25,8
	340	77,5	63	29,9	3,8			25,4
	345	77,5	68	34,3	3,4			24,4
	360	77,5	88	50	2,6			
Nonanal	303	80,0	22	6,6	12,1	-2027 -1571 -1500 -1100	13,8	26,8
	320	80,0	36	15,0	5,6			25,0
	340	80,0	55	28,8	3,6			24,8
	345	80,0	61,5	33,2	3,4			23,7
	360	80,0	80	50	2,4			

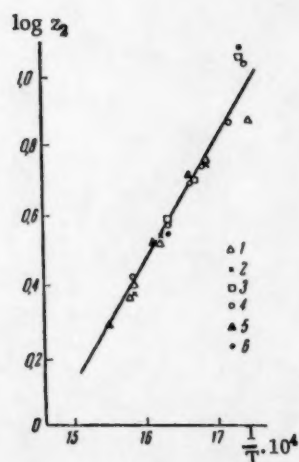


Fig. 1. Relation of $\log z_2$ to the reciprocal of the absolute temperature: 1) Ethyl alcohol; 2) pentyl alcohol; 3) hexyl alcohol; 4) heptyl alcohol; 5) octyl alcohol; 6) nonyl alcohol.

Nonyl Alcohol. The conversion of alcohol into aldehyde at 280-360° with $v = 1.4$ ml of alcohol in 5 minutes amounted to 7.7-62.7%. The relative adsorption coefficient of the aldehyde varied from 12.1 to 2.4 in the range 303-360° with $v = 1.4$ ml in 5 minutes.

From the results given above, it will be seen that, under the conditions used, normal primary alcohols are dehydrogenated at similar speeds. The values of the adsorption coefficients of the aldehydes are also close to one another. It was found that there is a logarithmic relation between z_2 and the reciprocal of the absolute temperature. The points for the normal primary alcohols investigated fit closely to a straight line (Fig. 1).

SUMMARY

The relative adsorption coefficients of aldehydes are a function of temperature; They fall with rise of temperature. To a first approximation, they do not depend on the chain length.

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EFFECT OF MOLECULAR STRUCTURE ON DEHYDROGENATION KINETICS IN THE CASE OF C₄ AND C₈ ALCOHOLS

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In the present paper, we consider the kinetics of the dehydrogenation of secondary alcohols of normal and branched structure (sec-butyl alcohol, 2-octanol, and 2,4-dimethyl-3-pentanol) and of branched primary alcohols (isobutyl alcohol and 2-ethyl-1-hexanol).

EXPERIMENTAL

The experimental procedure was the same as that described previously [1]. All the experiments were carried out over the same sample of catalyst. The experiments with secondary alcohols were carried out in the temperature range 270-380° with a feed of alcohol of 1-2.8 ml in 5 minutes. The relative adsorption coefficients z of the reaction products (ketones and aldehydes) were determined from the rates of dehydrogenation of their binary mixtures with alcohols under the same conditions and were calculated from Formula (3):

$$z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1},$$

in which m_0 and m are the rates of liberation of hydrogen in the passages at identical rates of pure reactant and of a $p\%$ mixture of the reactant with the substance for which z is being determined. The constants of the alcohols and aldehydes investigated are given in Table 1.

sec-Butyl Alcohol. In the range 265-330° at $v = 1.0$ ml in 5 minutes, the conversion of alcohol into ketone was 21.2-62.9% (Table 2). The relative adsorption coefficient of butanone varied with temperature from 1.7 at 280° to 1.0 at 330° (Table 4).

2-Octanol. The rate of dehydrogenation of the alcohol was measured in the temperature range 270-320° at a feed of alcohol of 1.8 ml in 5 minutes. The conversion of alcohol into ketone was 15.3-39.5% (Table 2). Under these conditions, the relative adsorption coefficient of the ketone varied from 1.9 at 270° to 0.8 at 320° (Table 4).

2,4-Dimethyl-3-pentanol. The conversion of the alcohol over the investigated temperature range of 260-360° at a feed of alcohol of 1.4 ml in 5 minutes was 4.7-72.4% (Table 2). The relative adsorption coefficient of 2,4-dimethyl-3-pentanone varied from 11.4 at 300° to 2.7 at 361° (Table 4).

Isobutyl Alcohol. In the range 300-380° with $v = 1.0$ ml of alcohol in 5 minutes the conversion of alcohol into aldehyde was 6.6-38.8% (Table 3). The relative adsorption coefficient of isobutyraldehyde varied from 8.7 at 320° to 1.9 at 380° (Table 4).

TABLE 1. Physical Constants of Alcohols, Aldehydes, and Ketones [2]

Substance	Starting substance			Data in literature		
	B.p. (°C)	d_4^{20}	n_D^{20}	B.p. (°C)	d_4^{20}	n_D^{20}
Alcohols						
sec-Butyl alcohol	98,5	0,8077	1,3972	99,5	0,8080	1,3972
2-Octanol	177,5	0,8191	1,4240	178,5	0,8193	1,4244
2,4-Dimethyl-3-pentanol	137,8-139	0,8291	1,4249	140	0,8288	1,4249
2-Ethyl-1-hexanol	182,8-183	0,8320	1,4318	181-184	0,83281	0,4328
Isobutyl alcohol	107,5	0,8034	1,3954	107,5	0,8046	1,3960
Ketones and Aldehydes						
Butanone	79,8	0,8400	1,3788	79,6	0,8058	1,3788
2-Octanone	172	0,8160	1,4165	171-173,5	0,8185	1,4162
2,4-Dimethyl-3-pentanone	124-125	0,8036	1,4010	125-126	0,8062	1,4001
Isobutyraldehyde	63,9	0,7940	1,3730	63-64	0,7938	1,3730
2-Ethylhexanal	161-162	0,8219	1,4170	162-165	0,8205	1,4150

TABLE 2. Dehydrogenation of Normal and Branched Secondary Alcohols

Alcohol	Temp. (°C)	Vol. of H ₂ (STP) liberated in 5 min (ml)	Deg. of dehydrogenation from vol. of H ₂ (%)	Analysis of gas (% by vol.)	
				CO ₂	H ₂
sec-Butyl alcohol (feed of 1 ml in 5 min.). Theoretical vol. of H ₂ from 1 ml 244.6 ml	265	52,0	21,2	0,2	99,6
	280	74,0	30,2	0,2	99,8
	305	115	47,0	0,2	99,8
	320	138,0	55,5	0,2	99,8
	340	173,0	70,6	0,2	99,8
2-Octanol (feed of 1.8 ml in 5 min.). Theoretical vol. of H ₂ from 1.8 ml 254.1 ml	270	39,0	15,3	0,2	99,8
	280	46,0	18,1	0,2	99,8
	300	69,0	27,1	0,2	99,8
	320	100,5	39,5	0,2	99,8
2,4-Dimethyl-3-pentanol (feed of 1.4 ml in 5 min.). Theoretical vol. of H ₂ from 1.4 ml 223.8 ml	283	39,9	17,8	Nil	Not determined
	300	63,0	28,2	0,2	99,8
	320,5	92,8	41,4	0,2	99,8
	340	121,4	54,2	0,2	99,8
	358	157,0	70,3	0,2	99,8

2-Ethyl-1-hexanol. The experiments were carried out in the range 300-380° at a feed of 1.4 ml in 5 minutes. The conversion of alcohol into aldehyde varied over this temperature range from 12.5 to 58% (Table 3). The relative adsorption coefficient of 2-ethylhexanol under these conditions varied from 27 at 300° to 4.0 at 380° (Table 4).

The results show that the rate of dehydrogenation of secondary alcohols falls with increase in molecular weight. Thus, sec-butyl alcohol is dehydrogenated more rapidly than 2-octanol. The rate of the dehydrogenation of the branched 2,4-dimethyl-3-pentanol is much greater than that of the normal sec-butyl alcohol. Branched primary alcohols are dehydrogenated at different rates. Thus the rate of dehydrogenation of 2-ethyl-1-hexanol is close in value to that of 2-octanol, but isobutyl alcohol is dehydrogenated more slowly than the normal primary butyl alcohol. It was found that for secondary alcohols there is a linear relation between $\log z_2$ and $1/T$: apart from $\log z_2$ for 2,4-dimethyl-3-pentanone, the points lie on a straight line (Fig. 1).

TABLE 3. Dehydrogenation of Branched Primary Alcohols

Alcohol	Temp. (°C)	Vol. of H ₂ (STP) libera- ted in 5 min. (ml)	Deg. of dehy- drogenation from vol. of H ₂ (%)	Analysis of gas (%) by vol.)	
				CO ₂	H ₂
Isobutyl alcohol (feed of 1 ml in 5 min). Theoretical vol. of H ₂ from 1 ml of alcohol 243.0 ml.	301	15,9	6,6	Her	100
	320	28,0	11,5	0,4	99,6
	340	44,0	18,1	0,6	99,4
	366	73,2	30,1	0,6	99,4
	385	108,0	44,5	0,4	99,4
	405	144,0	59,7	0,4	99,6
2-Ethyl-1-hexanol (feed of 1.4 ml in 5 min). Theoretical vol. of H ₂ from 1.4 ml of alcohol 200 ml. (Feed of 2.8 ml in 5 min). Theoretical vol. of H ₂ from 2.8 ml 400.1 ml.	300	25,0	12,5	Her	100
	320	38,0	19,0	0,2	99,8
	340	58,0	29,0	0,2	99,8
	360	82,0	41,0	0,4	99,6
	380	116,0	58,0	0,6	99,4
	360	190,6	47,6	0,2	99,8
	381	257,9	64,5	0,2	99,2
	412	369,6	92,4	0,6	99,4

TABLE 4. Adsorption Coefficients of Ketones and Aldehydes, and Thermodynamic Functions Calculated from These

Substance	Temp. (°C)	Alcohol content of mix- ture (%)	m_s	m	z^s	ΔF (cal)	ΔH (cal)	ΔS (cal/degree- mole)
1	2	3	4	5	6	7	8	9
Butanone	280	80	74	51,5	1,7	-582,3	8,4	16,2
	305	80	115	88,0	1,2	-228,0		14,9
	320	80	138	108,0	1,1	-112,0		14,3
	340	80	173	141,0	0,9	+128,2		13,5
2-Octanone	270	75	39	24,0	1,9	-582,3	11,3	21,5
	280	75	46	29,5	1,7			
	300	75	69	49,0	1,23			
	320	75	100,5	79,0	0,8			
2,4-Dimethyl- -3-pentanone	300	75	63	13,2	11,4	-2768	16,6	33,8
	320	75	92	28,4	6,8	-2210		31,6
	342	75	125	53,4	4,0	-1710		29,9
	361	75	161	85,4	2,7	-1200		28,1
Isobutyralde- hyde	320	75	28	7,2	8,7	-2546	17,3	33,5
	340	75	44	16,0	5,3	-2077		31,5
	360	75	66	34,0	2,85	-1316		29,4
	380	75	94,5	58,0	1,9	-832		27,8
2-Ethylhexanal	300	80	25,0	3,2	27,0	-3188	15,3	34,5
	320	80	38,0	7,6	16,0			
	340	80	58,0	16,5	10,0			
	360	80	82,0	30,3	6,8			
	380	80	116,0	58,0	4,0			

We express our thanks to A. P. Meshcheryakov for the presentation of 2-ethylhexanol.

SUMMARY

The relative adsorption coefficients of ketones are independent of chain length and increase greatly with increased branching of the chain.

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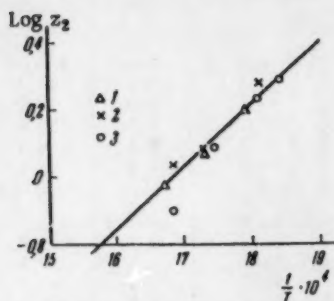


Fig. 1. Relation of $\log z_2$ to the reciprocal of absolute temperature: 1) isopropyl alcohol; 2) sec-butyl alcohol; 3) 2-octanol.

* Original Russian pagination. See C. B. translation.

SOLUBILITIES OF HEXANE, CYCLOHEXANE, AND BENZENE IN COMPRESSED ETHYLENE

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The solubilities of various hydrocarbons in saturated hydrocarbon gases compressed at temperatures above the critical point have received fairly detailed study, but there is very little information in the literature about the solvent powers of compressed (unliquefied) unsaturated hydrocarbon gases. A study of the solubilities of liquid hydrocarbons in ethylene is of interest from two points of view: First, compressed unsaturated hydrocarbon gases are beginning to find application as effective solvents in some industrial processes [1, 2]; second, data on the solvent powers of compressed unsaturated hydrocarbon gases with respect to liquid hydrocarbons of various kinds can be utilized in the development of the theory of intermolecular action in the gas phase.

EXPERIMENTAL

In the present investigation, the solubilities of hexane, cyclohexane, and benzene in compressed ethylene were studied. The physicochemical characteristics of these hydrocarbons are given in the table.

Hydrocarbon	B.p. (°C at 760 mm)	d_4^{20}	n_D^{20}	Molar volume (cc/mole)	Latent heat of vaporization* at b.p. (cal/mole)
Hexane	68,8	0,6601	1,3758	130,7	6900
Cyclohexane	30,9	0,7801	1,4271	108,1	7185
Benzene	79,5	0,8788	1,5017	88,9	7353

* Data from literature.

The ethylene used contained 2,9% ethane as impurity. Its critical temperature was 10,5°.

The solubilities of hexane, cyclohexane, and benzene were studied in a thermostatted equilibrium vessel with an internal electromagnetic stirrer by a known method, consisting in the taking of samples of the gas phase in equilibrium with the liquid phase under isobaric and isothermal conditions. The temperature in the equilibrium vessel was maintained constant within $\pm 0.05^\circ$. The pressure was determined with two pressure gauges covering different ranges of pressures. Pressures were measured accurately within 0.3%. The error in the determination of the concentration of solute in the gas phase did not exceed 0.002 (expressed as mole fraction).

The results of the solubility measurements on hexane, cyclohexane, and benzene are presented in the forms of graphs of $N = f(P)$ in Figures 1, 2, and 3. The graphs show that with rise in temperature, the mole fraction of liquid hydrocarbon in the gas phase increases. In the ethylene-hexane system, the left branch of the transition from

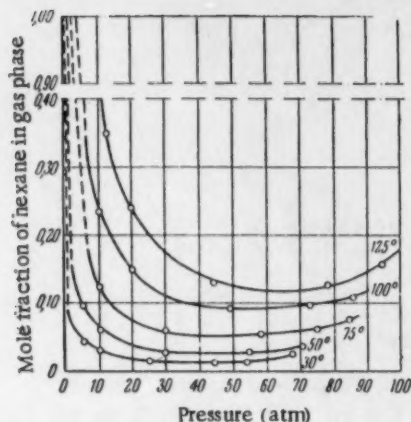


Fig. 1. Solubility isotherms for hexane in compressed ethylene.

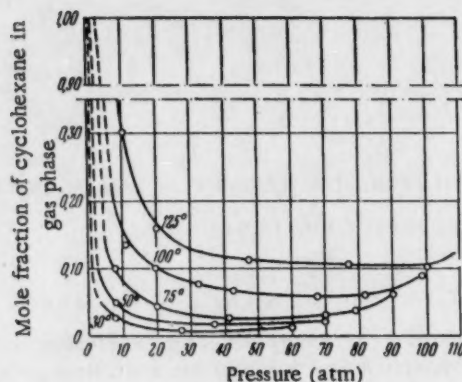


Fig. 2. Solubility isotherms of cyclohexane in compressed ethylene.

the curve to the right occurs over an ever-diminishing range of pressures as the temperature rises, and the minimum of the curve becomes more sharply defined. In the ethylene-cyclohexane and ethylene-benzene systems, this regularity is not observed.

The graphs (Figures 1-3) show that the solubility of hexane in ethylene is appreciably higher than the solubilities of cyclohexane and benzene at all temperatures investigated. The solubilities of cyclohexane and benzene in ethylene at 30°, 50°, 75°, and 100° are almost the same within the limits of experimental error, and only at 125° is the mole fraction of cyclohexane in the gas phase appreciably higher than that of benzene at the same pressure. This fact is undoubtedly associated with the natures of the investigated liquid hydrocarbons. Hexane consists of open-chain molecules. Comparison of the constants of hexane that indirectly characterize the molecular field with the same constants of benzene and cyclohexane (b.p., vapor pressure, molar volume, latent heat of vaporization, etc.) shows that the passage of hexane molecules into the gas phase can be effected with a smaller expenditure of energy than that spent in the passage of cyclohexane and benzene molecules into the gas phase. Comparison of the constants characterizing the molecular interactions of benzene and cyclohexane shows that for these hydrocarbons, the tendencies to pass into the gas phase at temperatures close to their boiling points are about the same.

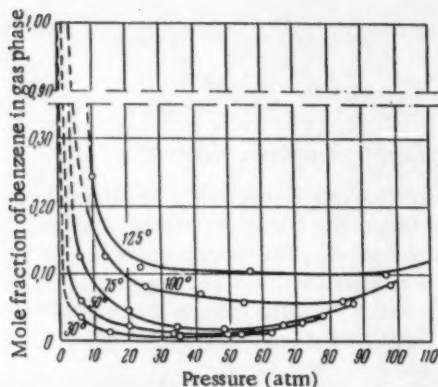


Fig. 3. Solubility isotherms of benzene in compressed ethylene.

We attempted to make use of Robin and Vodar's equation [3] in the calculation of the solubilities of hexane, cyclohexane, and benzene in ethylene. In this, we limited the equation to the second virial coefficient B_{12} , which expresses the interaction of a pair of different molecules. It was found that in the temperature range 30-75° and with pressures up to 10 atm, the solubility values calculated from this equation agree well with the values obtained experimentally. At higher pressures, this equation is quite unsuitable for the calculation of the solubilities of hexane, cyclohexane, and benzene in ethylene. It appears that in this case, it is necessary to take account of virial coefficients of higher order than the second.

Fig. 4 presents experimental data on the solubilities of hexane, cyclohexane, and benzene in the form of graphs of $\log m = f(P, t)$, in which m is the content of liquid hydrocarbon in the gas phase in g/cc of compressed ethylene. It will be seen from Fig. 4 that $\log m = f(P, t)$ isotherms are almost linear; the only exception is in the ethylene-hexane system at 75-125° with pressures ranging up to 10 atm.

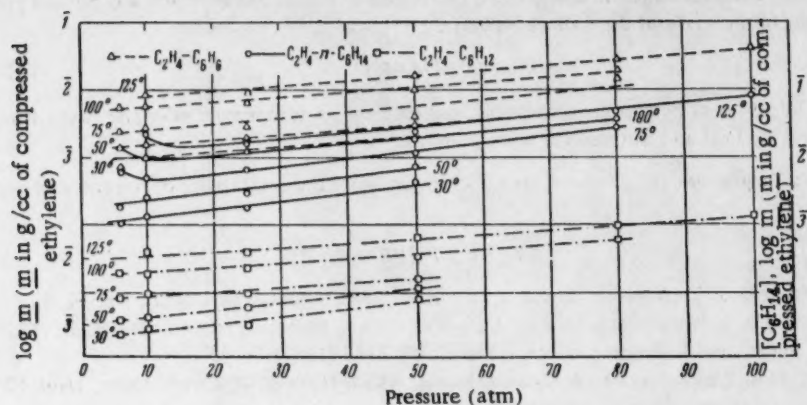


Fig. 4. Solubility isotherms of hexane, cyclohexane, and benzene in compressed ethylene.

We attempted to present the results of the investigation in the form of a series of equations, i.e., express $\log m = f(P, t)$ analytically. For the ethylene-hexane system, the equation has the form: $\log m = (-3.48752 + 0.01368t) + (0.015136 - 0.00006129t)P$. The application of this equation is limited to the temperature range 30-75° and to pressures up to 50 atm. The average error is 6%, and the maximum error does not exceed 10-12%.

For the ethylene-benzene system, the equation has the form: $\log m = (-3.5590 + 0.12376t) + (0.018232 - 0.00020942t)P$. The application of this equation is limited to the temperature range 30-75° and to pressures up to 50 atm. The average error in the determination of solubility from this equation is 7%, and the maximum error does not exceed 15%. It must be pointed out that the experimental data on this solubility of cyclohexane in ethylene can be expressed as an empirical equation like those given above only for narrower ranges of temperature and pressure.

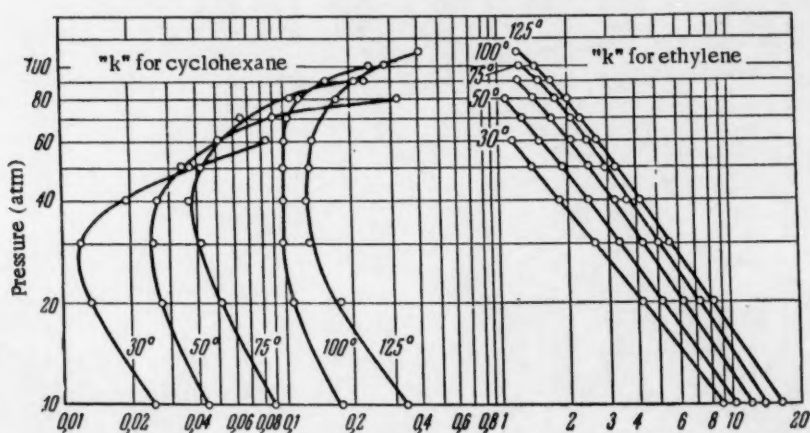


Fig. 5. Equilibrium constant, $k = \frac{y}{x}$

In Fig. 5, equilibrium constants $k = y/x = f(P, t)$ are given for ethylene and cyclohexane; here y and x are the mole fractions of the substance in the gas and liquid phases (when this diagram was printed previously [4], there was an error in the scale of the axis of ordinates).

SUMMARY

1. The solubilities of hexane, cyclohexane, and benzene in compressed ethylene were investigated in the temperature range 30-125° and at pressures up to 100 atm.

2. Empirical equations are proposed for the calculation of the solubilities of hexane and benzene in compressed ethylene.

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SOLUBILITIES OF ETHYLENE IN HEXANE, CYCLOHEXANE, AND BENZENE UNDER PRESSURE

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In view of the fact that compressed hydrocarbon gases are beginning to be applied as solvents in various processes in the chemical and petroleum-processing industries [1, 2], it is necessary to have information regarding the solubilities of individual unsaturated hydrocarbon gases in hydrocarbons of various classes at high pressures. Also, this information is necessary both for the calculation of the solubilities of mixtures of unsaturated hydrocarbon gases in liquids and for the development of the theory of the solubility of gases in liquids under pressure, which is still insufficiently advanced.

Substance	Constants				
	B.p. (°C at 760 mm)	d_4^{20}	n_D^{20}	Molar volume* (cc/mole)	Latent heat of vaporization* at b.p. (cal/mole)
Hexane	68,8°	0,6601	1,3758	130,7	6900
Cyclohexane	80,9	0,7801	1,4271	108,1	7185
Benzene	79,5	0,8788	1,5017	88,9	7353

*Data from literature.

In the present paper, we report results of a study of the solubilities of ethylene in liquid hexane, cyclohexane, and benzene at 35-150° under pressures of 100-120 atm. In choosing hydrocarbons of different nature but containing the same number of carbon atoms as solvents, we had the object of determining the effect of the nature of the solvent on the solubility of a given gas. Such information can be applied in the elucidation of the molecular mechanism of the solution of gases in liquids under pressure. The solubilities of ethylene in hexane, cyclohexane, and benzene under pressure were studied in the apparatus described in [3].

EXPERIMENTAL

The ethylene used in this investigation had a purity of 97.1%; it contained 2.9% of ethane as impurity. Its specific gravity with respect to air was 0.9748. The characteristics of the hydrocarbons are given in the table.

The method of investigating the solubility of ethylene in liquid hydrocarbons consisted in the determination of the saturation pressure and the corresponding specific volume for a series of mixtures of ethylene and liquid hydrocarbon of known composition. The exact value of the saturation pressure for each mixture investigated and the corresponding specific volume was determined from the break in $v = f(P, t)$ curves, which were plotted on large-scale diagrams. Curves for the solubilities of ethylene in hexane, cyclohexane, and benzene were constructed from the results and are presented in Figures 1-3. From these figures it will be seen that a crude linear

relation between the solubility of ethylene and pressure is found only in the ethylene-hexane system. In contrast, the ethylene-benzene system shows the greatest departure from the linear relation, even at high temperatures.

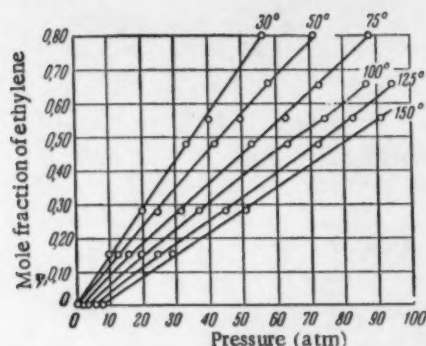


Fig. 1. Solubility isotherms for ethylene in hexane.

gas and solvent molecules. As we have investigated the solubilities of one particular gas in different liquids, we shall confine ourselves to a consideration of the factors in the secondary category. There are no data in the literature characterizing the interaction forces between ethylene molecules and molecules of hexane, cyclohexane, and benzene.

An idea of the molecular field of a liquid, which is a function of its nature, can be obtained indirectly from the values of the latent heat of vaporization, the molar volume, the surface tension, etc. The data in the table enable us to follow the changes in these constants among the hydrocarbons under consideration. It will be seen that in the series $n\text{-C}_6\text{H}_{14}$ — C_6H_{12} — C_6H_6 there is a lowering of molar volume and a rise in latent heat of vaporization. If we regard the mechanism of the solution of ethylene as being, to the first approximation, the incorporation of molecules of a gas into a complex of molecules of a liquid, on the basis of the data in the table, we may suppose that the solubility of ethylene should fall in the series hexane—cyclohexane—benzene.

The results of the investigation of the solubilities of ethylene in these liquids are in good agreement with this supposition. The experimentally determined specific volumes corresponding to saturation pressures at various temperatures were recalculated as molar volumes V_M . By way of example, in Fig. 4 we give the relation of the molar volume of the ethylene-cyclohexane system to the mole fraction N_2 of ethylene at 30°, 50°, 75°, 100°, and 125°. It will be seen from Fig. 4 that at 30° and 50° V_M diminishes linearly with increase in the ethylene content of the liquid phase right up to $N_2 = 0.65$ –0.70. With further increase in N_2 , the sign of the slope reverses and V_M rises with increase of N_2 at a given temperature; the rise is steeper the higher the temperature. An analogous relation of V_M to N_2 is observed also in the ethylene-benzene system. It must be pointed out, however, that for this system at $t = 30^\circ$ and 50° a linear fall in V_M with rise in N_2 occurs up to $N_2 = 0.55$ –0.65.

For the ethylene-hexane system, the linear reduction in molar volume with rise in the ethylene content of the solution at $t = 30^\circ$ and 50° is observed over the whole range of ethylene concentrations investigated. At higher temperatures, the character of the relation of V_M to N_2 is analogous to that described above.

The curves for the solubility of ethylene in cyclohexane have an intermediate character over the whole ranges of temperature and pressure investigated. The graphs (Figures 1-3) show that the solubility of ethylene in the hydrocarbons investigated falls with rise in temperature at constant pressure. At given temperature and pressure, the solubility of ethylene falls along the series hexane—cyclohexane—benzene.

It is interesting to trace the connection of the regularity observed in the solubilities of ethylene in hexane, cyclohexane, and benzene with the molecular constants of these hydrocarbons. In the theoretical treatment of questions of solubility of gases in liquids, it is necessary to account for: 1) interaction forces between molecules of the gas; 2) interaction forces between molecules of the liquid; and 3) interaction forces between molecules of dissolved

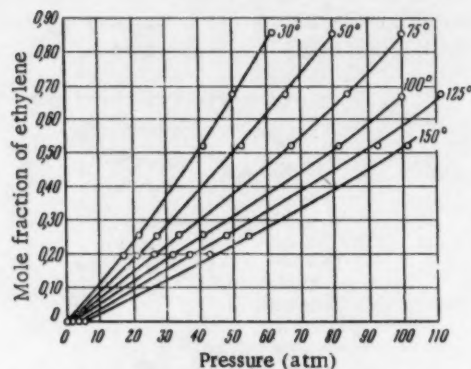


Fig. 2. Solubility isotherms for ethylene in cyclohexane.

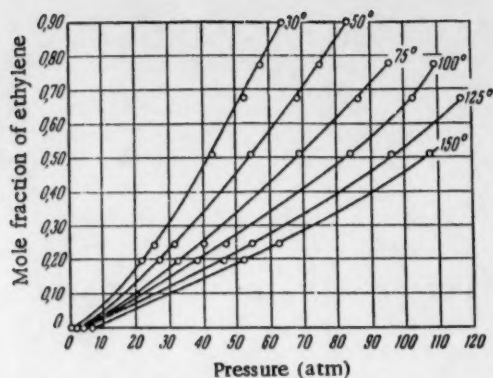


Fig. 3. Solubility isotherms for ethylene in benzene.

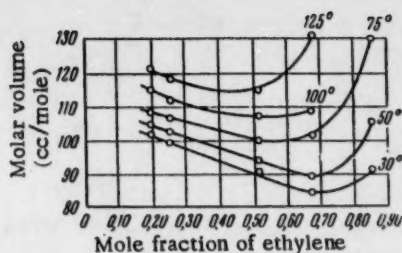


Fig. 4. Relation of the molar volume of a solution of ethylene in cyclohexane to the mole fraction of ethylene.

SUMMARY

1. The solubilities of ethylene in liquid hexane, cyclohexane, and benzene were investigated at 30-150° at pressures ranging up to 120 atm.
2. At a given temperature and pressure, the solubility of ethylene falls along the series $n\text{-C}_6\text{H}_{14}\text{-C}_6\text{H}_{12}\text{-C}_6\text{H}_6$.
3. Calculations were made of the molar volumes of mixtures, corresponding to saturation pressures at temperatures ranging from 30° to 125°.

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*Original Russian pagination. See C. B. translation.

TRANSFORMATION OF 1-HEXENE UNDER THE ACTION OF CARBON MONOXIDE AND HYDROGEN OVER A COBALT CATALYST

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Original article submitted July 7, 1959

It was earlier shown [1] that at atmospheric pressure and 190° 1-hexene remains almost unchanged when it is passed at a space velocity of 0.4 hr⁻¹ over the Co-clay catalyst usually used by us for the synthesis of hydrocarbons from olefins, hydrogen, and carbon monoxide. Under these conditions, 1-hexene in admixture with three molecular proportions of hydrogen is hydrogenated to an extent of about 60% to hexane and simultaneously undergoes disproportionation with respect to molecular weight with formation of higher-boiling hydrocarbons (C₇ and higher) with a boiling limit of 150° (7.6% on the weight of hexene taken) and of lower-boiling hydrocarbons, i.e., gaseous (4.4%) and liquid (11.7% of C₆). When CO is added to the C₆H₁₂-H₂ mixture, the disproportionation of hexene with respect to molecular weight is more marked and hydrogenation to hexane is not so prominent. In the reaction of a mixture of 51% of hexene, 42% of hydrogen, and 7% of carbon monoxide (7 : 6 : 1, Expt. 228/1), 22.6% (on weight of original olefin) of higher-boiling hydrocarbons (C₇ and higher) with a boiling limit of 296°, 8.2% of C₆ hydrocarbons, and 1% of hydrocarbon gases were formed. Hexene was hydrogenated to hexane to an extent of 20.4%.

In the present investigation, we had the object of studying the effect of an increased CO concentration on the course of the formation of hydrocarbons from 1-hexene, hydrogen, and carbon monoxide. The relative amounts of the components in the original vapor-gas mixture (the H₂/CO ratio was 2.2, and the CO content was 18%) were such that olefins of lower molecular weight (propene and 1-butene) scarcely reacted at all [2].

EXPERIMENTAL

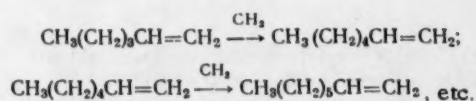
The apparatus and experimental procedure were the same as in the previous work [1]. 1-Hexene was prepared by thermal decomposition of hexyl acetate in a stream of nitrogen at 490-500° by the method proposed by Van Pelt and Wibaut [3], and it had: b.p. 63.4-63.5° (760 mm); d₄²⁰ 0.6732; n_D²⁰ 1.3882; bromine value 190, which corresponds to 99.6% unsaturates.

A Co-clay catalyst promoted with 18% of ThO₂ (calculated on metallic Co) was used in the work, and the volume of catalyst in the glass reaction tube, diameter 10 mm, was 30 ml. Before an experiment with hexene, the catalyst was treated at 190° with a 1 : 2 mixture of CO and H₂ until it attained maximum activity (the maximum yield of hydrocarbons was then 180 ml/m³ at a space velocity of 90 hr⁻¹). The reaction with a ternary mixture of 1-hexene, hydrogen, and carbon monoxide in which the contents of the components in the vapor-gas phase were 42, 40, and 18 moles per cent respectively (Expt. 229) was carried out at 190° at atmospheric pressure. From 177.4 ml of 1-hexene passed at a space velocity of 0.27 hr⁻¹, we obtained 170.5 ml of liquid catalyzate, 4.5 ml of reaction water, 14.4 liters of gas which was not condensed at -80° and had a composition of (% by vol.) 4.1 of CO₂, 2.0 of C_nH_{2n}, 35.2 of CO, 43.9 of H₂, and 14.8 of C_nH_{2n+2}, and 3.6 g of solid paraffin, which was removed from the catalyst when it was treated with hydrogen at 450°. Carbon monoxide reacted to the extent of 61.6%, and hydrogen reacted to the extent of 81.3%. The ratio of the amounts of H₂ and CO that reacted was

about 3 : 1. After being dried over anhydrous copper sulfate, the liquid catalyzate had d_4^{20} 0.6822; n_D^{20} 1.3932, and bromine value 139.8; 140 ml of it was fractionated through a column of 40-plate efficiency. The table gives the fractions collected and their properties. C_3 - C_4 hydrocarbons were almost completely absent from the liquid catalyzate; the content of C_5 hydrocarbons was only 0.9%, that of higher-boiling hydrocarbons containing seven or more carbons was 20.6%, and that of hexane was 12.6% by weight on the 1-hexene passed. The hydrocarbon gases (C_1 - C_2) present in the final gas amounted to 1.4% by weight on the original olefin.

Fraction	Boiling limits ($^{\circ}C$)	Content in catalyzate (% by vol.)	d_4^{20}	n_D^{20}	Bromine value	Content of unsaturateds (%)	C_n
I	30—44	1,0	0,6644	1,3870	184,5	97,1	C_5
II	44—63	6,3	0,6723	1,3880	188,1	99,0	C_6
III	63—64	15,1	0,6735	1,3877	181,4	95,3	C_6
IV	64—70	56,8	0,6724	1,3865	147,1	77,4	C_6
V	70—320	19,1	0,7373	1,4163	68,6	54,0	C_7 - C_{17}

It follows from the results that the higher-boiling hydrocarbons could not be formed solely by the Orlov-Fisher-Tropsch reaction. About 90% of these hydrocarbons was formed by reaction in which 1-hexene took part, and only about 10% by synthesis from CO and H_2 . For each mole of CO entering into reaction with formation of higher hydrocarbons, 0.95 of a mole of 1-hexene was drawn into this reaction. About 56% of the higher-boiling hydrocarbons could be formed by the hydrocondensation of 1-hexene with carbon monoxide by successive steps of chain growth with the aid of carbons from carbon monoxide:



Comparison of the results of this investigation with those obtained previously [1] shows that, with increase in the CO content of the original vapor-gas mixture from 7 to 18% at an H_2 /CO ratio of 2.2, the tendency for 1-hexene to form higher hydrocarbons under the action of a mixture of carbon monoxide and hydrogen is diminished only slightly. However, increase in the CO concentration caused a sharp reduction in the yield of hydrocarbons boiling lower than hexene and hexane, and also in the yields of hexane and hydrocarbon gases. Under these conditions, propene and 1-butene, unlike 1-hexene, scarcely react at all in the way indicated above, when the same proportions of olefin, hydrogen, and carbon monoxide are used, whether the catalyst is promoted or unpromoted [4]. Individual members of the olefin series, therefore, may show a specificity that at present can be revealed only by experimental means and not by extrapolation from results obtained with lower-boiling homologs.

SUMMARY

1. A study was made of the effect of a high concentration of carbon monoxide on the course of the formation of hydrocarbons from 1-hexene, hydrogen, and carbon monoxide.
2. When the H_2 : CO ratio in the original vapor-gas mixture is changed from 6 to 2.2, the yield of higher-boiling hydrocarbons is reduced only slightly, but the formation of lower-boiling hydrocarbons is almost completely suppressed.
3. The effect of an increased concentration of carbon monoxide in reactions in which propene or 1-butene take part is different from its effect in the reaction with 1-hexene.

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*Original Russian pagination. See C. B. translation.

ACTION OF HYDRAZINE AND PHENYLHYDRAZINE ON DIALKYLTHIOBORINIC ESTERS

B. M. Mikhailov and Yu. N. Bubnov

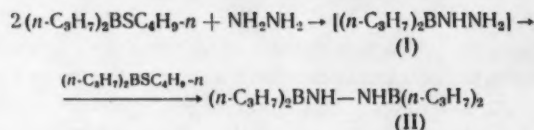
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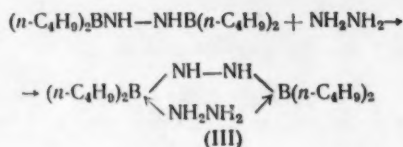
Original article submitted July 7, 1959

We have recently found that butyl dibutylthioborinate reacts with hydrazine and with phenylhydrazine with formation respectively of 1,2-bisdibutylborinohydrazine and 1-dibutylborino-2-phenylhydrazine [1]. In the present paper, we report the results of a further study of the reactions of dialkylthioborinic esters with hydrazine and phenylhydrazine.

When a mixture of two equivalents of butyl dipropylthioborinate and one equivalent of hydrazine is heated to 50-110°, 1,2-bisdipropylborinohydrazine (II) is obtained in 89% yield. The reaction clearly passes through the stage of (dipropylborino)hydrazine (I), which is more active towards the dialkylthioborinic ester than hydrazine.

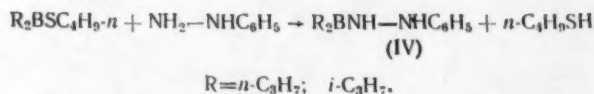


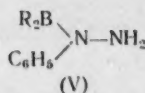
Compounds of type (I) are not obtained by reaction of a 1,2-bisdialkylborinohydrazine with excess of hydrazine. Thus, mixture of the previously obtained 1,2-bisdibutylborinohydrazine [1] with hydrazine gives a crystalline complex (III) which decomposes to its components when warmed:



We did not succeed in effecting further replacement of hydrogen atoms by dialkylborino groups in the compound (II): When (II) was heated with a dialkylthioborinic ester, it was unaffected.

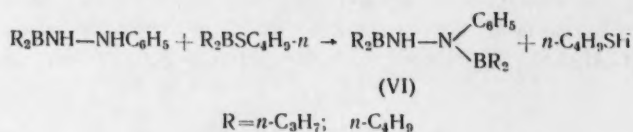
At 100° dialkylthioborinic esters react with phenylhydrazine with formation of 1-dialkylborino-2-phenylhydrazines (IV):





The compounds obtained are assigned the structure (IV) rather than (V) on the basis of their reaction with the thio ester which requires a higher temperature than hydrazine, phenylhydrazine, or a (dialkylborino)hydrazine (I), which contain unsubstituted amino groups.

As the experiments showed, a 1-dialkylborino-2-phenylhydrazine (IV) will react with a dialkylthioborinic ester only at 150-200° with formation of a 1,2-bisdialkylborino-1-phenylhydrazine (VI). The resulting compounds are assigned the structure (VI) on the basis of the observation referred to previously, according to which hydrogen atoms attached to nitrogen which is also attached to a dialkylborino group are not further substituted under the action of dialkylthioborinic esters.



When solutions of 1-dialkylborino-2-phenylhydrazines in carbon tetrachloride or methyl iodide are allowed to stand, they acquire an intense blue or green color, respectively, and give precipitates.

EXPERIMENTAL

All operations were carried out in an atmosphere of nitrogen.

Butyl Diisopropylthioborinate [2]. 1-Butanethiol (14 ml, 0.134 mole) was added to triisopropylborine (18.5 g, 0.132 mole), and a considerable rise in temperature occurred. The reaction mixture was heated at 150° for 15 minutes. Gas amounting to 3100 ml was liberated, and this contained 132 millimoles of propane, 0.38 millimoles of propene, and 0.38 millimoles of hydrogen. Distillation gave 17.5 g (76.9%) of butyl diisopropylthioborinate: b.p. 83-84° (8 mm); n_D^{20} 1.4582; d_4^{20} 0.8253. Found: C 64.22; 64.59; H 12.58; 12.55; B 5.91; 5.96%. $\text{C}_{10}\text{H}_{23}\text{BS}$. Calculated: C 64.51; H 12.45; B 5.81%.

1,2-Bisdipropylborinohydrazine (II, R = n-C₃H₇). A mixture of 12.6 g (0.068 mole) of butyl dipropylthioborinate [2] and 1.1 ml (0.034 mole) of hydrazine was heated in a vacuum (34 mm) for 15 minutes with simultaneous distillation of the thiol (the bath temperature was raised gradually from 50° to 100°). We obtained 6 g (89%) of 1-butanethiol and 6.05 g (79.1%) of 1,2-bisdipropylborinohydrazine; b.p. 121-122° (9 mm); n_D^{20} 1.4421; d_4^{20} 0.7966. Found: C 64.56; H 13.32; 13.28; B 9.37; 9.42%. $\text{C}_{12}\text{H}_{30}\text{B}_2\text{N}_2$. Calculated: C 64.33; H 13.50; B 9.66%.

1-Diisopropylborino-2-phenylhydrazine (IV, R = i-C₃H₇). A mixture of 13.9 g (0.075 mole) of butyl diisopropylthioborinate and 7.4 ml (0.07 mole) of phenylhydrazine was heated for 25 minutes in a vacuum (150 mm) at 100-105°. We obtained 6.72 g (90%) of 1-butanethiol and 13.4 g (87.6%) of 1-diisopropylborino-2-phenylhydrazine; b.p. 89-90° (0.035 mm); n_D^{20} 1.5151; d_4^{20} 0.9181. Found: C 70.93; 70.92; H 10.45; 10.53; B 5.15; 5.17%. $\text{C}_{12}\text{H}_{21}\text{BH}_2$. Calculated: C 70.60; H 10.37; B 5.30%.

1-Dipropylborino-2-phenylhydrazine (IV, R = n-C₃H₇). From 13.9 g (0.074 mole) of butyl dipropylthioborinate and 7.4 ml (0.07 mole) of phenylhydrazine, we similarly obtained 6.98 g (93.4%) of 1-butanethiol and 13.8 g (90.8%) of 1-dipropylborino-2-phenylhydrazine; b.p. 94-95° (0.03 mm); n_D^{20} 1.5165; d_4^{20} 0.9196. Found: C 70.98; 70.90; H 10.69; 10.70; B 5.54%. $\text{C}_{12}\text{H}_{21}\text{BN}_2$. Calculated: C 70.61; H 10.37; B 5.30%.

1,2-Bisdipropylborino-1-phenylhydrazine (VI, R = n-C₃H₇). A mixture of 7.15 g (0.036 mole) of 1-dipropylborino-2-phenylhydrazine and 9.9 ml (0.042 mole) of butyl dipropylthioborinate was heated for one hour in a vacuum (160 mm) at 180-190° (bath temperature); 2.65 g of 1-butanethiol was liberated. Vacuum fractionation gave 7.12 g (68.5%) of 1,2-bisdipropylborino-1-phenylhydrazine, b.p. 115-116° (0.08 mm). After refractionation the substance had: b.p. 105-106° (0.04 mm); $n_D^{21.5}$ 1.4901; $d_4^{21.5}$ 0.872. Found: C 71.79; 71.93; H 11.61; 11.57; B 6.99; 7.55%. C₁₈H₃₄B₂N₂. Calculated: C 72.03; H 11.42; B 7.21%.

1,2-Bisdibutylborino-1-phenylhydrazine (VI, R = n-C₄H₉). A mixture of 10.8 g (0.047 mole) of 1-dibutylborino-2-phenylhydrazine [1] and 12.1 g (0.057 mole) of butyl dibutylthioborinate was heated for 30 minutes in a vacuum (25 mm) at a bath temperature of 100-200° with simultaneous distillation of the thiol formed. We obtained 4.31 g of 1-butanethiol and 13.04 g (78.9%) of 1,2-bisdibutylborino-1-phenylhydrazine; b.p. 132-133.5° (0.03 mm); n_D^{20} 1.4883; d_4^{20} 0.8678. Found: C 73.86; 74.19; H 11.95; 11.78; B 6.15; 6.08%. C₂₂H₄₂B₂N₂. Calculated: C 74.17; H 11.88; B 6.07%.

All organoboron derivatives of hydrazine are colorless liquids, soluble in organic solvents and readily hydrolyzed and oxidized.

Hydrazine Complex of 1,2-Bisdibutylborinohydrazine (III, R = n-C₄H₉). A mixture of 2.37 g of 1,2-bisdibutylborinohydrazine and 0.28 g of hydrazine was found to crystallize out completely in the course of one week. The product was washed with isopentane and vacuum-dried. We obtained 2.42 g (88%) of the hydrazine complex of 1,2-bisdibutylborinohydrazine in the form of colorless crystals, m.p. 39-40.5°. Found: C 61.18; 60.78; H 13.71; 13.91; B 7.23; 6.49%. C₁₆H₃₂B₂N₄. Calculated: C 61.55; H 13.56; B 6.93%. The substance is readily oxidized by atmospheric oxygen.

SUMMARY

1. Dialkylthioborinic esters react with hydrazine and with phenylhydrazine with formation, respectively, of 1,2-bisdialkylborinohydrazines and 1-dialkylborino-2-phenylhydrazines.
2. When heated with dialkylthioborinic esters, 1-dialkylborino-2-phenylhydrazines react with formation of 1,2-bisdialkylborino-1-phenylhydrazines.
3. With hydrazine, 1,2-bisdialkylborinohydrazines form crystalline complexes which decompose when heated.

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REACTIONS OF TRIALKYLBORINES WITH HYDRAZINE AND PHENYLHYDRAZINE

B. M. Mikhailov and Yu. N. Bubnov

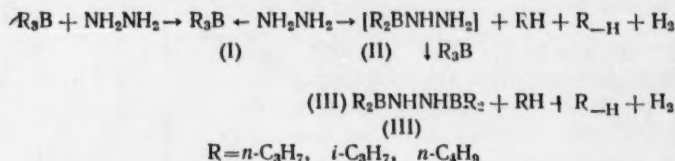
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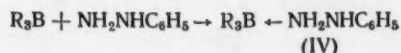
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Trialkylborines react when heated with compounds containing active hydrogen, e.g., with water [1, 2], with alcohols [1, 2], with amines [1, 2], and with thiols [2]. It was of interest to investigate the reactions of trialkylborines with hydrazine and phenylhydrazine and in this way to determine the possibility of preparing hydrazine derivatives of organoboron compounds which we had synthesized earlier by the reaction of dialkylthio-borine esters with hydrazine and with phenylhydrazine [3, 4].

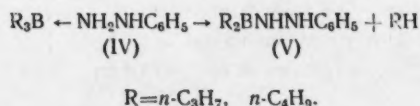
When trialkylborines are mixed with hydrazine in equimolecular amounts, there is a considerable rise in the temperature of the reaction mixture and complex compounds (I) are obtained in which the components are present in the ratio of 1 : 1. Molecular-weight determinations showed that they are partially dissociated in solution. When heated to 150-170°, the complex compounds are converted into 1,2-bisdialkylborinohydrazines (III) and gaseous substances, namely paraffins, olefins, and hydrogen. The relative amounts of the gaseous products depends on the temperature and the duration of the experiment (see table).



The reaction between trialkylborines and phenylhydrazine, which is accompanied by the evolution of much heat, leads to the formation of crystalline complex compounds (IV) containing the components in the ratio of 1 : 1; in benzene solution, they are partially dissociated into their components. Thus, the molecular weight of the complex of tripropylborine with phenylhydrazine, determined in benzene, was found to be 196 (duplicate 197), though the calculated value was 248.



The complexes (IV) undergo thermal decomposition at temperatures as low as 80-90° with formation of 1-dialkylborino-2-phenylhydrazine (V) and gaseous products consisting almost entirely of saturated hydrocarbons, but for the completion of the reaction, it is necessary to heat at 150-160° toward the end.



The mechanism of the reactions of trialkylborines with compounds containing mobile hydrogen and accompanied by the elimination of a saturated hydrocarbon or a mixture of saturated and unsaturated hydrocarbons and hydrogen has been discussed by us previously [2]. All organoboron compounds of hydrazine are readily oxidized in the air, are hydrolyzed by water, and react with alcohols; in the last case, as previously [3], we were unable to obtain (dipropylborino)hydrazine by the alcoholysis of 1,2-bisdipropylborinohydrazine (II), probably because of its symmetrization or greater reactivity as compared with the diboron-substituted hydrazine (III).

EXPERIMENTAL

All operations were carried out in an atmosphere of nitrogen.

Hydrazine Complex of Tripropylborine. Hydrazine (0.1 mole) was added to tripropylborine (0.1 mole). Much heat was evolved, and a thick colorless liquid was formed which consisted of the hydrazine complex of tripropylborine. Cryoscopic molecular-weight determination in benzene gave values of 145 and 151. Calculated for $(n\text{-C}_3\text{H}_7)_3\text{B}:\text{N}_2\text{H}_4$, 172.

Hydrazine (0.5 mole) was added to tripropylborine (0.1 mole). Cryoscopic molecular-weight determination in benzene gave values of 154 and 145. Calculated for $2(n\text{-C}_3\text{H}_7)_3\text{B}:\text{N}_2\text{H}_4$, 312.

Phenylhydrazine Complex of Tripropylborine. Phenylhydrazine (12 g, 0.11 mole) was added to tripropylborine (15.46 g, 0.11 mole). The mixture, which grew very hot (about 100°), gave a white precipitate when cooled. Washing with 100 ml of isopentane gave 26.4 g (96%) of the complex, m.p. 59-5-60.5°. After recrystallization from isopentane, the substance had m.p. 54.5-55.5°. Found: C 72.54; 72.87; H 12.21; 12.46; B 4.51; 4.43%; mol. wt. 197.4, 195.6. $\text{C}_{16}\text{H}_{12}\text{BN}_2$. Calculated: C 72.58; H 11.78; B 4.36%; mol. wt. 248.

Reactions of Trialkylborines with Hydrazine. A mixture of 0.1 mole of the trialkylborine and 0.05 mole of hydrazine was prepared in a three-necked flask fitted with thermometer, dropping funnel, tube for the introduction of nitrogen, and reflux condenser, which was connected with a gas holder. There was a spontaneous rise in temperature to 80-100°. The reaction mixture was heated in a metal bath at 150-180° for 1-1.5 hours (until gaseous products ceased to be liberated), and was then vacuum-fractionated. The yields of reaction products and the compositions of the gases formed are given in the table.

1,2-Bisdiisopropylborinohydrazine has the following properties: b.p. 78-79° (2 mm); n_D^{20} 1.4430; d_4^{20} 0.7951. Found: C 64.31; 64.62; H 13.46; 13.50; B 9.63; 9.54%. $\text{C}_{12}\text{H}_{30}\text{B}_2\text{N}_2$. Calculated: C 64.33; H 13.50; B 9.66%.

Reactions of Trialkylborines with Phenylhydrazine. The procedure was similar to that described above. The reaction time was 20-80 minutes, and the temperature was 150-170°. The results of the experiments are given in the table.

Action of Butyl Alcohol on 1,2-Bisdipropylborinohydrazine. A solution of 2.58 g (0.011 mole) of 1,2-bisdipropylborinohydrazine in 1.03 g (0.015 mole) of butyl alcohol was heated for ten minutes at 130°, and then

No.	R ₁ B		Hydrazine		Reaction temperature (°C)	Reaction time (hours)	Gaseous reaction products (moles)			Reaction product	Yield (%)	B.p. in °C (p in mm)
	Formula	Moles	Formula	Moles			C _n H _{2n+2}	C _n H _{2n}	H ₂			
1	(i-C ₃ H ₇) ₃ B	0.067	N ₂ H ₄	0.033	150—170	1	0.0134	0.0367	0.0376	[(i-C ₃ H ₇) ₂ BNH] ₂	62	78—79(2)
2	(n-C ₃ H ₇) ₃ B	0.084	N ₂ H ₄	0.04	150—170	1.5	0.0195	0.0428	0.0446	[(n-C ₃ H ₇) ₂ BNH] ₂	53.6	123—125(1)
3	(n-C ₃ H ₇) ₃ B	0.0133	N ₂ H ₄	0.067	155—175	1.25	0.051	0.0497	0.0524	[(n-C ₃ H ₇) ₂ BNH] ₂	62.2	109—110(5)
	(n-C ₃ H ₇) ₃ B	0.1	N ₂ H ₄	0.05	150—170	1	0.392	0.0251	0.030	[(n-C ₃ H ₇) ₂ BNH] ₂	59.1	117—118(1)
	(n-C ₃ H ₇) ₃ B	0.046	N ₂ H ₄	0.024	155—160	1.4	0.0382	0.0198	0.0226	[(n-C ₃ H ₇) ₂ BNH] ₂	54.9	128—130(2,4)
4	(n-C ₃ H ₇) ₃ B	0.087	N ₂ H ₄	0.044	160—180	1.5	0.025	0.029	0.036	[(n-C ₃ H ₇) ₂ BNH] ₂	55.6	129.5—131(2,5)
	(n-C ₃ H ₇) ₃ B	0.065	C ₆ H ₅ NHNH ₂	0.069	160—170	0.5	0.0603	0.0016	0.0014	[(n-C ₃ H ₇) ₂ BNHNHC ₆ H ₅] ^[3]	70	95—98(0.035)
5	(n-C ₃ H ₇) ₃ B	0.087	C ₆ H ₅ NHNH ₂	0.089	150—160	0.4	0.0664	0.0022	0.0022	[(n-C ₃ H ₇) ₂ BNHNHC ₆ H ₅] ^[5]	62	112—113(0.08)

a mixture of hydrazine and butyl alcohol was distilled off at a bath temperature of 160-170°. We obtained 0.86 g of butyl dipropylborinate, b.p. 74-76° (14 mm) and n_D^{20} 1.4150, and 0.61 g of unchanged 1,2-bisdipropylborinohydrazine, b.p. 128-129° (14 mm).

A solution of 2.18 g (0.010 mole) of 1,2-bisdipropylborinohydrazine in 2.2 g (0.029 mole) of butyl alcohol was heated for ten minutes at 125-130°. A mixture of hydrazine and butyl alcohol was distilled off under reduced pressure (100 mm). We obtained 2.54 g of butyl dipropylborinate, b.p. 74-76° (15 mm) and n_D^{20} 1.4142. The literature [5] gives: b.p. 76-76.5° (15 mm); n_D^{20} 1.4133.

SUMMARY

With hydrazine and phenylhydrazine trialkylborines form complex compounds which decompose when heated with formation, respectively, of 1,2-bisdialkylborinohydrazines and 1-dialkylborino-2-phenylhydrazines.

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SYNTHESIS OF 3-ETHOXY-1-PHENYL-1,3-BUTADIENE

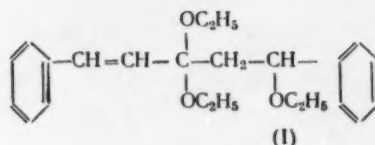
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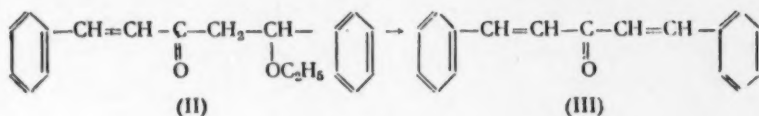
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 2, pp. 372-373, February, 1960

Original article submitted July 7, 1959

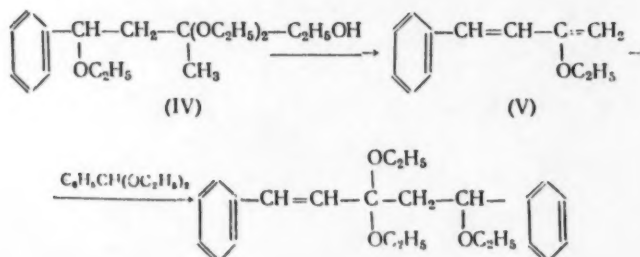
We have shown previously [1] that the reaction of benzaldehyde diethyl acetal with ethyl isopropenylether in presence of zinc chloride gives a high yield of 1,3,3-triethoxy-1-phenylbutane (IV). Further investigation showed that the higher fraction formed in this reaction, b.p. 190-200° (3 mm), contains 3,3,5-triethoxy-1,5-diphenyl-1-pentene (I):



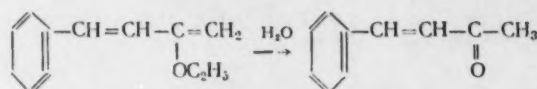
This was shown as follows. Treatment of this fraction with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of 5-ethoxy-1,5-diphenyl-1-penten-3-one (II). The structure of the ketone (II) was established by its conversion into 1,5-diphenyl-1,4-pentadien-3-one (III):



The formation of 3,3,5-triethoxy-1,5-diphenyl-1-pentene (I) in the reaction of benzaldehyde diethyl acetal with ethyl isopropenyl ether can be represented as the result of the following secondary reactions of the primary condensation product, 1,3,5-triethoxy-1-phenylbutane (IV):



The possibility of the formation of 3-ethoxy-1-phenyl-1,3-butadiene (V) in the course of the reaction was proved by its preparation from 1,3,3-triethoxy-1-phenylbutane by the elimination of the elements of alcohol, which proceeds readily under the action of zinc chloride and some other reagents of acidic character. The 3-ethoxy-1-phenyl-1,3-butadiene formed polymerizes extremely readily, and it could therefore be isolated only by carrying out the elimination of alcohol under special conditions (by the action of p-toluenesulfonic acid in presence of organic bases). The structure of 3-ethoxy-1-phenyl-1,3-butadiene was proved by its conversion by hydrolysis into 4-phenyl-3-buten-2-one (benzylideneacetone) (VI):



3-Ethoxy-1-phenyl-1,3-butadiene polymerizes to a clear solid, soluble in benzene and insoluble in alcohol.

EXPERIMENTAL

3,3,5-Triethoxy-1,5-diphenyl-1-pentene (I). In the reaction, which was carried out by the previously described method [1], we took 88 g (0.5 mole) of benzaldehyde diethyl acetal, 5 ml of a 5% ethereal solution of ZnCl_2 , and 17.2 g (0.2 mole) of ethyl isopropenyl ether. In the fractionation of the products, apart from 1,3,3-triethoxy-1-phenylbutane (IV), b.p. 111-113° (3 mm), we obtained 5 g of a fraction of b.p. 190-200° (3 mm), which contained 3,3,5-triethoxy-1,5-diphenyl-1-pentene. By treatment of this fraction with 2,4-dinitrophenylhydrazine sulfate in alcohol, we obtained a mixture of hydrazines, and by fractional crystallization of this from alcohol, we isolated the 2,4-dinitrophenylhydrazone of 5-ethoxy-1,5-diphenyl-1-penten-3-one in the form of light orange needles, m.p. 174.5-175°. Found: C 65.73; 65.50; H 5.19; 5.11; N 12.59; 12.73%. $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_5$. Calculated: C 65.21; H 5.25; N 12.17%.

5-Ethoxy-1,5-diphenyl-1-penten-3-one (II). The fraction of b.p. 190-200° (3 mm) (3.5 g) was hydrolyzed with 1% H_3PO_4 by the method described in the literature [2]. We obtained an oily product which contained 5-ethoxy-1,5-diphenyl-1-penten-3-one. By the elimination of the elements of alcohol by the action of p-toluenesulfonic acid in toluene [2], we obtained 1 g of 1,5-diphenyl-1,4-pentadien-3-one, m.p. 111-112°. The literature [3] gives m.p. 112-112.5°.

3-Ethoxy-1-phenyl-1,3-butadiene (V). p-Toluenesulfonic acid (0.01 g) and a few drops of quinoline were added to 10 g (0.375 mole) of 1,3,3-triethoxy-1-phenylbutane. The mixture was cautiously heated in a vacuum (2 mm). When the elimination of alcohol started, the pressure in the system rose to 8-10 mm. When the pressure fell again to 2 mm, the heating was stopped and the reaction mixture was dissolved in ether; the solution was washed with sodium bicarbonate solution and dried over potassium carbonate. Fractionation gave 5 g (76.5%) of 3-ethoxy-1-phenyl-1,3-butadiene; b.p. 80-82° (2 mm); d_4^{20} 0.9789; n_D^{20} 1.5823. Found: C 82.54; 82.59; H 8.01; 8.14%. $\text{C}_{12}\text{H}_{14}\text{O}$. Calculated: C 82.72; H 8.10%.

Shaking of 3-ethoxy-1-phenyl-1,3-butadiene with 5% HCl gave 4-phenyl-3-buten-2-one (benzylideneacetone), m.p. 40-42°. The literature [4] gives m.p. 40-42°. By treatment of a solution of 3-ethoxy-1-phenyl-1,3-butadiene in pyridine with a solution of semicarbazide hydrochloride, we obtained the semicarbazone of 4-phenyl-3-buten-2-one, m.p. 184-185°. The literature [5] gives m.p. 185°.

SUMMARY

1. By the action of catalytic amounts of p-toluenesulfonic acid in quinoline on 1,3,3-triethoxy-1-phenylbutane, 3-ethoxy-1-phenyl-1,3-butadiene is obtained.
2. Under the action of acidic reagents 3-ethoxy-1-phenyl-1,3-butadiene readily polymerizes with formation of a solid polymer.

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DIPOLE MOMENTS OF SOME ORGANOSILICON COMPOUNDS

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We have measured the dipole moments of seven organosilicon compounds by the heterodyne method at 25° in benzene. Extrapolated values of total polarization were calculated from Hedestrand's formula. As we have already shown in another investigation [1], atom polarization has some significance in the case of organosilicon compounds, and it cannot be neglected since it amounts to 15-20% of the electron polarization in some cases. It can lead to an error in the dipole moment, particularly in the case of molecules that are not very polar. Hence, for the compounds measured, we calculated atom polarization by comparison with known values of P_A for various silicon compounds on the assumption of approximate additivity of this quantity for compounds that are similar in structure. Instead of extrapolated values of the electron polarization, in the calculation, we used refraction for the yellow sodium line in order to compensate to some extent for the values of atom polarization, which were probably a little low. The experimental and calculated data obtained are given in the table, which lists the total polarization, the molecular refraction, the atom polarization, and the dipole moment for each of the compounds measured.

Compound	Formula	\bar{P} (cc)	R_D (cc)	P_A (cc)	$\mu \times 10^{18}$
I	$(CH_3)_3SiCH=CHSi(CH_3)_3$	67,9	58,8	9,1	0
II	$(C_2H_5)_3SiCH=CHSi(C_2H_5)_3$	94,4	85,7	8,7	0
III	$Cl_3SiCH=CHSiCl_3$	72,3	55,6	10-11	0,5-0,6
IV	$(CH_3)_3SiCH_2C_6H_4COCH_3-p$	313,9	64,6	7,0	3,41
V	$(CH_3)_3SiCH_2CH_2C_6H_4COCH_3-p$	289,5	69,2	7,4	3,20
VI	$(CH_3)_3SiCH_2CH_2CH_2C_6H_5$	70,5	62,9	6,0	0,3
VII	$(CH_3)_3SiCH_2C_6H_4Br-p$	162,0	62,2	6,5	2,12

The first three of the compounds given in the table are symmetrical silane derivatives of ethylene in which rotation around the central $C=C$ bond is restricted. For these compounds, there are two probable configurations of the molecules corresponding to maximum interaction of the π -electrons of the $C=C$ bond, namely, the trans- and cis-configurations. The measurements showed that bistrimethylsilyl and bistriethylsilyl ethylenes have zero dipole moments ($\mu = 0$). This indicates that the trialkylsilyl groups occupy trans positions in these compounds. These compounds have a high atom polarization, $P-P_E$ = about 9 cc. The trans configuration of these compounds is the more probable one because in the cis position, the silyl groups must repel one another on account of their large size and the closeness with which they must approach one another, if the valence angles are to be preserved. All positions other than the cis and trans positions are of low probability in compounds with a double bond. The third compound, $Cl_3SiCH=CHSiCl_3$, should also have the trans configuration on account of

steric hindrance and strong repulsion in the *cis* position (the distance between the centers of the chlorine atoms should be 2 Å, whereas the sum of the covalent radii of these atoms is 1.98 Å). However, even if we assume that the atom polarization of this molecule is about 10-11 cc, the dipole moment is still not less than 0.5-0.6 D. It is possible that the double-bond character of the C=C bond is considerably reduced by the withdrawal of electrons to the chlorine atoms of SiCl₃ groups and also by the possibility of the participation in 3d orbitals in the case of silicon (Si state). If these suggestions are correct, there may be breakdown of coplanarity around the C=C bond and incomplete compensation of the C-Si bond and the bonds of SiCl₃. It is possible, therefore, that the compound (III) does not possess a truly coplanar *trans* form.

The moment of the compound (CH₃)₃SiCH₂CH₂C₆H₄COCH₃-p (V) is 0.21 D less than that of the compound (IV). We observed an analogous effect in the case of the *p*-nitrophenyl and *p*-bromophenyl derivatives [1]. This is probably to be explained by alternating polarity [2] in the chain of bonds, which is observed also in other organosilicon compounds. The same property is found also in the compound (CH₃)₃SiCH₂CH₂C₆H₅ (VI), which has a moment of about 0.3 D, i.e., somewhat greater than that of the analogous β-compound (μ = 0), which is also in accord with the hypothesis of alternating polarity in these compounds. It should be noted that the difference between α- and β-derivatives is 0.55 D. The effect of the silicon atom on substituents diminishes rapidly as they become more remote. It is interesting to compare the compound (CH₃)₃SiCH₂C₆H₄Br-*p* (VII) with the analogous triethyl derivative (μ = 2.08 D); their dipole moments are fairly close together.

SUMMARY

1. The dipole moments of seven organosilicon compounds were measured.
2. It was found that 1,2-bis(trimethylsilyl)-, 1,2-bis(triethylsilyl)-, and 1,2-bis(trichlorosilyl) ethylenes have *trans*-configurations.
3. The presence of alternating polarity was detected in the compounds (CH₃)₃SiCH₂C₆H₄COCH₃-*p* and (CH₃)₃SiCH₂CH₂C₆H₄COCH₃-*p*.
4. The effect of the silicon atom on a substituent diminishes with lengthening of the hydrocarbon chain.

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SIMPLE METHOD OF PREPARING PURE PLATINUM DIOXIDE

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The investigation of platinum and its oxides of interest, not only from the point of view of catalysis. It has been shown [1] that oxide layers can be particularly clearly detected on platinum and that the layers can be slowly evaporated in a vacuum and will slowly re-form with increase in the oxygen pressure, which makes platinum a suitable subject for the investigation of surface phenomena on metals. Platinum dioxide is interesting also in that it, like montmorillonite minerals, is incapable of forming a three-dimensional lattice and shows only hk0 reflections in electronographic investigation.

Because of the lack of success of attempts to prepare the dioxide by the dehydration of platinum oxide hydrates the usual method during the last 25 years has become the method of the direct oxidation of platinum black by oxygen at high pressures. It has been noted [2] that in all such cases, a mixture of various products is obtained, so that for a long time, the structure of platinum dioxide remained unelucidated. Only by the cathodic atomization of platinum in an oxygen atmosphere was it possible to obtain a product that was sufficiently pure for a study of its structure to be possible. It was shown [1] that platinum dioxide forms well defined two-dimensional layers in which, the constant of the hexagonal lattice is $a = 3.10 \text{ \AA}$ and that the layers are formed as the result of the condensation of PtO_2 molecules, which arises in collisions of rapidly moving platinum atoms with oxygen molecules.

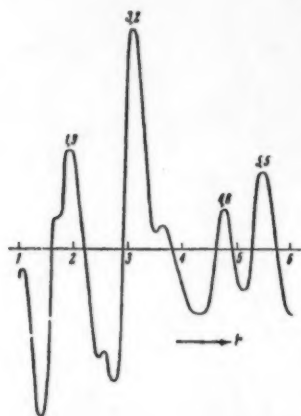


Fig. 1

The possibility of such a reaction in the gas phase is confirmed by the following considerations. It is known that the oxygen molecule, in which the bond energy is 119 kcal/mole, is able to capture electrons. The addition of the first electron lowers the bond energy to about 90 kcal/mole, and the addition of the second to 50 kcal/mole [3]. This residual bond energy is found to be already insufficient to hold two oxygen ions of like charge together, and therefore, each of them takes still another electron with formation of the stable doubly-charged O^{2-} ion. On the other hand, it is characteristic of the platinum atom that it can donate four electrons. It may therefore be supposed that reaction in the gas phase will proceed even in absence of active oxygen species which could be formed in a glow discharge.

To realize the required conditions, a platinum spiral was brought to red heat by passage of a current in a flask containing oxygen at a pressure of about 0.1 mm. A black film then formed on the walls of the flask. X-ray and electron diffraction data confirmed our views (Fig. 2 and table). From these data a radial-distribution curve was constructed (Fig. 1); this also confirms the



Fig. 2.

correctness of our previous discussion on the structure of this product, including the presence of a third dimension (axis $c = 4.8$ Å), even if only in a rudimentary form. Our previous suggestions concerning the hindrance of the growth of the crystals in the third dimension by oxygen layers adsorbed by the platinum-oxygen plates still, therefore, remain valid.

Results Derived from X-ray Photographs of Platinum Dioxide

Intensities of reflections	Interplanar distances	Reflection indices	Lattice periods (Å)		Intensities of reflections	Interplanar distances	Reflection indices	Lattice periods (Å)	
			a	c				a	c
100	2,69	100	3,11	4,8	25	0,74	310	3,10	
25	2,35	101			10	0,67	400	3,09	
100	1,55	110	3,10	4,9	12	0,61	320	3,08	
25	1,48	111			12	0,58	410	3,08	
50	1,34	200	3,10		6	0,52	330	3,11	
50	1,02	210	3,11		6	0,50	420	3,09	
50	0,89	300	3,10		6	0,48	510	3,08	
25	0,78	220	3,11		2	0,44	600	3,09	

Note. All $hk0$ reflections are equally sharp; slow falling in the intensities of the reflections as the angles increase is almost inappreciable; hkl reflections are slightly broadened; in addition to all these reflections, there are two long broad arcs with an azimuth at about 50° and belong to (111) planes of metal platinum, which is present in very small amount.

Reduction of the product with hydrogen at 400° gave the formula $PtO_{2.98}$. The excess of oxygen can be regarded as a sign of adsorption.

SUMMARY

1. PtO_2 molecules are readily formed in the collision of rapidly moving platinum atoms with free oxygen molecules, and, by condensing on the walls of the glass vessel, which is at room temperature, they readily form the known hexagonal lattice of this compound.

2. At an oxygen pressure of about 10^{-1} mm in a flask having a volume of about 200 cc, the deposit obtained contains an insignificant amount of unchanged metal.

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LETTERS TO THE EDITOR

NEW CASE OF THE FORMATION OF A 5 α ,6 α -EPOXY RING IN THE ANDROSTANE SERIES

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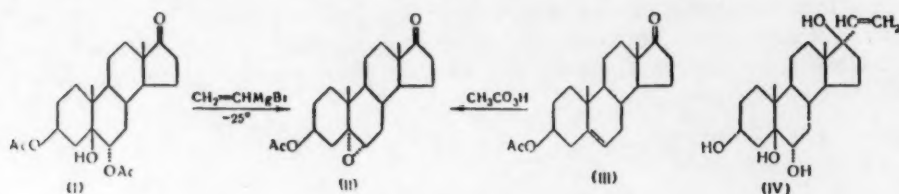
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While working on the synthesis of analogs of corticosteroids, we met an interesting case of the unusual formation of a 5 α ,6 α -epoxy ring: this was observed in the reaction of vinylmagnesium bromide with 3 β ,5 β ,6 α -tri-hydroxy-5 β -androstan-17-one (a trans-5,6-diol) (I) [1] in tetrahydrofuran [2]. The α -epoxide (II) then formed showed no depression of melting point in a mixture test with a known sample [3].

The expected 17 α -vinyl-5 β -androstan-3 β ,5 β ,6 α ,17 β -tetrol (IV) was not isolated. It is interesting that the triol diacetate (V) with the *cis* configuration of the hydroxyls at C-5 and C-6 [4] does not form a 5,6-epoxide under these conditions. In this case, the main product is a substance of m.p. 188-189°, which corresponds in analysis to 17 α -vinyl-5 α -androstan-3 β ,5 α ,6 α ,17 β -tetrol 3,6-diacetate (VI). A mixture with the 5 β ,6 β -epoxide (VII) [3], which has m.p. 186° and is epimeric at C-5 and C-6 to the epoxide (II), melted at 150°. In some experiments the formation of the 17 α -vinyl derivatives with free 3 β - and 6 α -hydroxy groups was observed.



Treatment of the acetic ester of the androst-5-en-7-one (III) with vinylmagnesium bromide gave a 70% yield of 17 α -vinylandrost-5-en-3 β ,17 β -diol (VIII), m.p. 182-183°, which was obtained previously in another way [5]. Under these conditions, the α -epoxide (II) does not give the Normant reaction.

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CURRENT EVENTS

SESSION OF THE DIVISION OF CHEMICAL SCIENCES, ACADEMY OF SCIENCES,
USSR, OCTOBER 15-16, 1959

L. G. Makarova

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In connection with the sixtieth anniversary of the birth of Academician Aleksandr Nikolaevich Nesmeyanov, President of the Academy of Sciences of the USSR and Director of the Institute of Heteroorganic Compounds, on October 15-16, 1959, a joint Session was held in Moscow of the Division of Chemical Sciences and the Scientific Council of the Institute of Heteroorganic Compounds.

The Session, which was held in the Institute of Organic Chemistry, was opened by Academician M. M. Shemyakin, who, after extending a cordial welcome to Academician A. N. Nesmeyanov, described him as the leader of the greatest school of chemists in the Soviet Union. Academician Shemyakin pointed out the wide range of scientific interests of Nesmeyanov from his brilliant investigations in theoretical organic chemistry and his syntheses based on 2-chlorovinyl ketones to his work leading to the large-scale production of macromolecular compounds, which now finds practical application.

The meeting was then addressed by Academician A. N. Nesmeyanov. His address was concerned with his work on the synthesis of diarylhalogenonium and triaryloxonium compounds and their properties. This field, which has been vigorously developed recently by Nesmeyanov, is reminiscent of his early investigations on the decomposition of the double compounds of diazonium salts and mercuric iodide, which give diaryliodonium salts by thermal decomposition. As shown recently, the thermal decomposition of the double salt formed by an arenediazonium bromide and mercuric bromide gives a diarylbromonium salt. The investigations on diarylhalogenonium and triaryloxonium salts were preceded by studies of the mechanism of the decomposition of arenediazonium and diaryliodonium salts. As a result of these investigations, it was found that, depending on the nature of the anion, arenediazonium and diaryliodonium salts may decompose not only homolytically, but also heterolytically. Heterolytic decomposition with formation of an aryl cation occurs with arenediazonium and diaryliodonium fluoborates. By the arylation of bromobenzene, chlorobenzene, and dibenzofuran with an aryl cation formed in the decomposition of an arenediazonium fluoborate, previously unknown diarylbromonium, diarylchloronium, and triaryloxonium salts were prepared. The properties and reactions of these very interesting compounds were extensively studied. It was shown that the stability of these compounds depends on the nature of the anion. It was found that the newly discovered diarylhalogenonium salts decompose and can arylate both by the heterolytic mechanism (arylation of the anions of salts and of amines) and also by the homolytic mechanism (arylation of metals). Triaryloxonium salts have an unexpectedly high stability: They decompose only at high temperatures and have little tendency to arylate. The behavior of triphenyloxonium and diarylhalogenonium salts in nitration shows that the diphenyloxonium group is an orientant of the first type, whereas the arylhalogenonium group orients electrophilic attack both in the meta position and in the para position.

A communication about the methods of synthesizing heteroorganic compounds developed by Nesmeyanov's school was made by R. Kh. Freidlina, Corresponding Member of the Academy. She discussed the devising of various methods of synthesis ("chemical ways of communication"), which Nesmeyanov regards as one of the most

important tasks of the chemistry of heteroorganic compounds. As a result of investigations over many years, Nesmeyanov's school has developed ways for the mutual conversion of organic compounds of many of the elements from almost all groups of the periodic system. In Nesmeyanov's investigations, the development of methods of synthesis is closely associated with the investigation of reaction mechanism. Nesmeyanov made extensive use of different mechanisms of cleavage of chemical bonds in the molecule in work on synthesis. Thus, the "onium" method of synthesis, which was developed by Nesmeyanov, permits the use of both homolytic (synthesis of organometallic compounds) and heterolytic (synthesis of diarylhalogenonium and triaryloxonium compounds, etc.) types of breakdown of onium compounds. Different mechanisms of exchange reactions of heteroorganic compounds with substances of the electrophilic, nucleophilic, and free-radical types are made use of in the synthesis of new heteroorganic compounds. Nesmeyanov is not confined to the narrow fields of particular questions of synthesis. The problems of synthesis being resolved by Nesmeyanov are primarily dictated by the practical needs of socialist construction. On the other hand, in the choice of these problems, Nesmeyanov is guided by profound study of the relation between the structure of an atom and its ability to form a heteroorganic compound.

In her paper entitled *The Diazo Synthesis of Organometallic Compounds*, Doctor Chem. Sci. L. G. Makarova described the great contribution made to science by the discovery by Nesmeyanov in 1929 of the universal method of synthesizing aromatic organometallic compounds, i.e., the method of double diazonium salts, or the diazo method, which consists in the decomposition of double salts formed from arene diazonium salts and metal halides by the action of a reducing agent. Developed in the first place for organomercury compounds, the diazo method permitted the preparation of these compounds with the most varied substituents in the aromatic nucleus, and was extended also to the synthesis of organomercury compounds of the heterocyclic, and more recently also the alicyclic and aliphatic series. The diazo method was further developed for the synthesis of aromatic compounds of other metals, namely antimony, arsenic, bismuth, thallium, tin, germanium, lead, and also selenium. It was shown that the diazo method opened up wide possibilities for the preparation of various types of organometallic compounds. The wide possibilities opened up by the diazo method for the synthesis of various groups of organomercury compounds, which are the key substances among the organometallic compounds, made it possible to use these compounds for the preparation of previously unknown types of aromatic compounds of zinc, tin, aluminum, thallium, lead, and germanium. Nesmeyanov's school has extensively developed variants of the diazo method for the synthesis of organometallic compounds, which enables one to select the best way of synthesizing an organic compound of a given metal by the diazo method.

Investigations on the diazo method prompted investigations aimed at elucidating its mechanism.

A. N. Nesmeyanov and the speaker have shown that diazonium, and also other onium compounds can decompose both homolytically and heterolytically with formation of aryl cations. The heterolytic decomposition of arene diazonium salts which was effected for the first time, was extensively applied for synthetic purposes. It was proved that the presence of metals converts the heterolytic decomposition of diazonium salts into homolytic decomposition, so that it must be assumed that the synthesis of organometallic compounds by the diazo method also proceeds homolytically.

In his paper entitled *Stereochemistry of Electrophilic and Homolytic Substitution at Saturated and Ethylenic Carbon Atoms*, O. A. Reutov, Corresponding Member of the Academy, described the results of investigations carried out by two groups of Nesmeyanov's students: Doctor Chem. Sci. A. E. Borisov and co-workers at the Institute of Heteroorganic Compounds, and the speaker and co-workers at the Moscow State University. As a result of a study of numerous mutual conversions of 2-chlorovinyl and isopropenyl cis- and trans-organometallic compounds of mercury, antimony, tin, thallium, and lead, it was shown that these reactions proceed with preservation of stereochemical configuration. This permitted A. N. Nesmeyanov and A. E. Borisov to state a rule concerning the preservation of geometric configuration in electrophilic and homolytic substitutions at an olefin carbon atom. This rule later received direct confirmation in the study of electrophilic and homolytic isotopic exchange with chlorovinyl compounds of mercury. The mechanism of electrophilic substitutions at a saturated carbon atom was studied. From a study of homolytic isotopic exchange between organomercury salts and metallic mercury, it was concluded that the configuration is preserved also in homolytic reactions at a saturated carbon atom.

The last communication at the session of October 15 was read by É. G. Perevalova, Candidate Chem. Sci., on her behalf and on behalf of N. A. Vol'kenau, N. S. Kochetkova, and V. A. Sazonova; it concerned investigations on ferrocene carried out under Nesmeyanov's guidance. The chemical properties of the peculiar ferrocene

system have been extensively and thoroughly studied by Nesmeyanov and co-workers. Extensive investigations have been made of the numerous substitutions of hydrogen atoms in ferrocene, which prove its aromatic character. It was shown that ferrocene readily enters into electrophilic and homolytic substitutions. A study was made of mercuration, metalation with alkylolithiums and alkylsodiums, Friedel-Crafts acylation, sulfonation, and arylation of ferrocene, and also of the substituted ferrocenes obtained. By further reactions of the substituted ferrocenes obtained, numerous ferrocene derivatives were synthesized: alkylferrocenes, ferrocene-carboxylic and -boronic acids, hydroxyferrocenes, selenium derivatives of ferrocene, ferrocenylamine, azoferrocene, haloferrocenes, and biferrocene. The effect of substituents on the reactivity of the ferrocene nucleus was determined. It was found that the effects of electron-donating and electron-accepting substituents are analogous to the effects of these substituents on the reactivity of benzene. This analogy with benzene was confirmed by a study of the basicity constants of ferrocenylamine and ferrocenylanilines and the dissociation constant of ferrocenylphenol. A study of the dissociation constants of ferrocenecarboxylic acid and substituted ferrocenecarboxylic acids showed the presence of the previously unknown phenomenon of transmission of conjugation through a metal atom.

The session of October 16 was opened by Academician M. I. Kabachnik, who read a paper on Dual Reactivity and Tautomerism. In this interesting paper, the speaker showed that, on the basis of systematic experimental investigations, Nesmeyanov had introduced some clarity in an important branch of theoretical organic chemistry concerned with the extremely involved problem of the dual reactivity of organic compounds and tautomerism. Nesmeyanov's investigations showed that dual reactivity and tautomerism are two completely different phenomena. Tautomerism is due to the equilibrium of isomers; it may be the cause of dual reactivity, but the latter can arise also for other, more general causes associated with conjugation. On the basis of a study of the properties of quasicomplex compounds, Nesmeyanov introduced the concept of the conjugation of single and multiple bonds, which was later extended to the explanation of the dual reactivity of metal derivatives of tautomeric systems. It was shown that the conjugation of single bonds is an extremely general phenomenon in organic chemistry. As early as 1950, Nesmeyanov had reviewed the extensive material of organic chemistry from the new point of view and had traced the manifestations of conjugation in various reactions of organic substances.

A. N. Nesmeyanov and M. I. Kabachnik formulated the now extremely widely known systematics of conjugation (π - π , π - σ , σ - σ , p - π , p - σ , p - p conjugation). The concept of the conjugation of single bonds enabled Nesmeyanov to predict and then to find a series of reactions in quite new directions, which included reactions in which a substance imitates the reactivity of its nonexistent tautomer and forms a series of derivatives. On the suggestion of Nesmeyanov, this type of reaction is said to proceed "with transfer of the reaction center". It was here that he found the general principle of dual reactivity that does not depend on tautomerism. The basic principles of tautomerism, which were found in the acid-base properties of tautomers, were developed. For the most important case, prototropy, tautomeric equilibrium is subject to the laws of acid-base protolytic equilibrium, the general laws of which were formulated by M. I. Kabachnik. The phenomenon of tautomerism arises as a consequence of the dual reactivity of the "common ion". New methods of investigation were developed, one of which was based on the stereospecificity of the reactions of geometric isomers. It has been shown in M. I. Kabachnik's laboratory that in the case of "pseudomers" dual reactivity arises solely by the mechanism of transfer of reaction center. In M. I. Kabachnik's opinion, the problem of tautomerism and dual reactivity is not only a theoretical problem of chemistry, but also a problem of branches of chemistry that are important from the practical point of view: organic dyes, polymers, medicinals; it is also one of the problems arising in the consideration of many of the most important biological structures.

V. N. Kost reviewed the study of the telomerization of ethylene and polymers at the Institute of Heteroorganic Compounds. In recent years, Nesmeyanov and co-workers have made an extensive study of telomerization, which is controlled polymerization leading to substances of "moderate" molecular weight, intermediate between polymers and monomers. An extensive study was made of the already known telomerization of ethylene with carbon tetrachloride and chloroform, which leads to a series of previously unknown α, α, α -trichloro- and $\alpha, \alpha, \alpha, \omega$ -tetrachloro-alkanes, which formed the starting points for the synthesis of a variety of compounds. A simple method was developed for the preparation of ω -amino carboxylic acids and this lies at the basis of the industrial synthesis of 7-aminoheptanoic and 9-aminononanoic acids, the polycondensation of which gave the new polyamide fibers "enant" and "pelargon", which have several advantages over "kapron". A simple method of synthesizing α -amino acids was developed, and also methods for higher dicarboxylic and hydroxy carboxylic

acids which are of interest for the perfumery industry. In the course of this work investigations of general interest for organic chemistry were carried out. At the end of the report demonstrations on the fiber "enant" and on articles made from this fiber were carried out.

E. Ts. Chukovskaya reported on the telomerization of olefins with silanes, which she studied under the guidance of Nesmeyanov. The thermal telomerization of olefins with silanes containing an Si-H bond was effected, and also telomerization in presence of a wide range of catalysts, which led to a simple and convenient method of preparing the previously difficultly accessible dialkyldichlorosilanes, and also alkyltrichlorosilanes. On the basis of these reactions various thermally stable polymers can be synthesized.

O. B. Nogina, Candidate Chem. Sci., read a paper on The Synthesis and Properties of Alkoxy Derivatives of Titanium. In the field of the chemistry of transition elements work is going on under the guidance of Nesmeyanov on the alkoxy derivatives of titanium. In this field, methods have been developed for the synthesis of various classes of derivatives of quadrivalent titanium, and methods for their mutual conversion have been studied. From tetraalkyl titanate derivatives of tervalent titanium have been prepared, and from these have been prepared previously unknown monomeric dialkoxytitanium oxides, compounds containing a π -bond between a transition element and oxygen, which is rare in the chemistry of organometallic compounds. The products of addition to these of silicon and titanium esters form the bricks from which heterochain polymers are constructed. Some of the compounds obtained have valuable properties in practice. In the study of alkoxy derivatives of titanium, a new, interesting physical phenomenon was observed: the disaggregation of associated alkoxy derivatives of titanium with time.

Doctor Chem. Sci. N. K. Kochetkov discussed synthesis on the basis of 2-chlorovinyl ketones. These substances are prepared in a very simple way from acetylene and acid chlorides, and, because of their high and very varied reactivity, they are key compounds in organic synthesis in the aliphatic, aromatic, and particularly heterocyclic series. The synthesis of aliphatic compounds is based on the replacement of the chlorine atom in 2-chlorovinyl ketones by other groups. Their use in the alicyclic series arises from the fact that 2-chlorovinyl ketones are active dienophiles. The condensation of 2-chlorovinyl ketones with compounds of the type of acetoacetic ester leads to substituted salicylic acids. A method based on 2-chlorovinyl ketones has been developed for the synthesis of alkylnaphthalenes. The most varied applications of 2-chlorovinyl ketones have been in the synthesis of heterocyclic compounds. Five-membered heterocycles have been prepared: derivatives of pyrazole and isoxazole. Pyridine derivatives are among the six-membered heterocycles prepared. This far from exhausts the possibilities opened up by 2-chlorovinyl ketones in organic synthesis. Some of the substances obtained are starting materials for the synthesis of pharmacologically active preparations.

M. I. Rybinskaya, Candidate Chem. Sci., reported on the synthesis of heterocycles containing an onium hetero atom from 2-chlorovinyl ketones. With 2-chlorovinyl ketones as starting point, the preparation of benzopyrylium, naphthopyrylium, and flavylium salts, among which one was a natural product (an anthocyanidin) was effected in various ways. The syntheses (from 2-chlorovinyl ketones) of heterocyclic compounds containing a quaternary nitrogen in the cycle are of particular interest. The speaker reported ring-closure reactions which she had carried out with the aid of 2-chlorovinyl ketones and their derivatives and which led to the synthesis of substituted dehydroquinolizinium salts and the previously unknown 1-aza- and 1,9-diaza- analogs of dehydroquinolizinium salts.

In a short final address Academician A. N. Nesmeyanov thanked the authors for the papers presented.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTLL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashglz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhtI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.- Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

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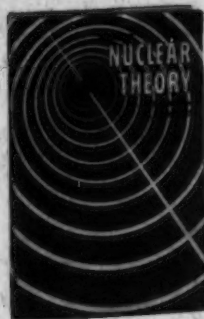
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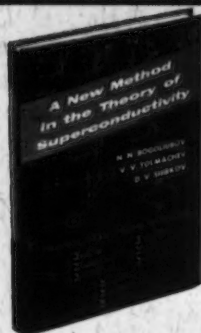
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